Harmonic voltage response to AC current in the nonlinear conductivity of iridium oxide $Ca_5Ir_3O_{12}$

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Abstract

We have carried out harmonic voltage response experiments by application of AC current along the c-axis of $Ca_5Ir_3O_{12}$, which has a nonlinear electrical conductivity in a non-ordered state. This AC current method can allow us to investigate a detail of the nonlinear conductivity by application of small current. We observed the harmonics up to 7th order below 200 K. The results reveal that the nonlinear conductivity exists even in application of current close to zero. In addition, the temperature dependence of the resistance R_0 estimated at the zero current limit is expressed by ln $R_0 \propto T^{-2/3}$, which is explained by an adaptation of Efros-Shklovskii variable range hopping or Fogler-Teber-Shklovskii variable range hopping. As a field assisted motion of charge career occurs in hopping conduction, from this analysis result, the nonlinear conductivity comes form the field-assisted hopping conduction.

Keywords:
iridates, frustration, nonlinear conductivity, variable range hopping

1. Introduction

Recent studies of $5d$ electrons systems have revealed a strong spin-orbit interaction (SOI) plays an important role in its magnetic and transport properties [1, 2, 3]. In particular, the magnetic and transport properties of Ir oxides with Ir^{4+} ($5d^5$) is characterized by the strong SOI and a moderate amount of correlations between the $5d$ electrons. There has been an increasing interest in Ir oxides with geometrical frustration because of their attractive magnetic and transport properties, such as Kitaev spin liquid in A_2IrO_3, spontaneous Hall effect at zero field in $Pr_2Ir_2O_7$, metal-insulator transitions with all-in all-out ordering in $Ln_2Ir_2O_7$ [4, 5, 6, 7, 8].

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Recently, nonlinear electrical conductivity in $Ca_5Ir_3O_{12}$ was discovered in the non-ordered state [9]. Nonlinear conductivity is often observed in the ordered states such as CDW, SDW, and charge-ordered phase in low-dimensional materials [12, 13, 14]. In some Ir and Ru oxides such as $BaIrO_3$ and Ca_2RuO_4, nonlinear conductivity is also observed below their magnetic ordering temperature [15, 16]. Although nonlinear conductivity of Sr_2IrO_4 is observed even above its antiferromagnetic ordering temperature, it is not clear whether the effect of self-heating is fully considered in the experiment [17]. On the other hand, $Ca_5Ir_3O_{12}$ has a nonlinear conductivity in the non-ordered state even while taking the influence of self-heating into consideration; the origin of nonlinear conductivity is not clear.

In this study, in order to investigate a detail of the nonlinear electrical conductivity of $Ca_5Ir_3O_{12}$, we carried out harmonic voltage response experiments by application of AC current along the c-axis of $Ca_5Ir_3O_{12}$; this AC current method can allow us to investigate a detail of the nonlinear conductivity by application of small current. $Ca_5Ir_3O_{12}$ has a hexagonal structure with noncentrosymmetric space group of $P\overline{6}2m$ (No. 189) [10, 11]. In the structure, one-dimensional (1D) chains of the edge-sharing IrO_6 octahedra form triangular lattices in the c-plane. The average valence of Ir ions in $Ca_5Ir_3O_{12}$ is +4.67, so Ir^{4+} and Ir^{5+} exist in a ratio of 1:2. This situation can lead to the geometric frustration of electric charge on both the triangular lattice in c-plane and 1D chains along the c-axis. It is reported that $Ca_5Ir_3O_{12}$ exhibits an antiferromagnetic below 7.8 K and a second-order phase transition at 105 K [11]; the origin of this phase transition at 105 K is not clear at present.

In this paper, we will report the results of harmonic voltage response experiments by AC current method. We have succeeded to observe the harmonics up to 7th order below 200 K. The results reveals that the nonlinear conductivity exists even in application of current close to zero. In addition, we will discuss the temperature dependence of the resistance R_0 estimated at the zero current limit from the view point of variable range hopping conduction.

2. Experimental Procedures

Single crystals of $Ca_5Ir_3O_{12}$ were grown by the $CaCl_2$ flux method as reported previously [9]. In this study, the same single crystal which had been used in Ref. [9] was used. The sample was fixed to the copper plate, which was insulated using Kapton tape with GE varnish. The terminal was fixed by using silver paste. The sample was located in a cryostat evacuated in a vacuum state.

Small electrical energy applied to sample is needed to eliminate an influence of self-heating because nonlinear conductivity can be observed due to self-heating. A pulse current method is one of the methods. However, it can be suggested as one of problems in this method that measurement accuracy deteriorates when small current is applied. On the other hand, in harmonic voltage response experiments, we can clearly confirm the nonlinear conductivity because a presence of harmonics means distortion of waveform. Therefore, we used AC current method to investigate a detail of the nonlinear conductivity by application of small current.

Figure 1 shows a schematic of measuring circuit. In this measurements, the sine-wave current was applied by using an AC and DC current source (Keithley 6221), and the temperature of copper plate with sample was well stabilized by GM refrigerator with PID control. The harmonic voltage response by application of sine-wave current was measured by Lock-in amplifier (NF Corp. LI5640). We inserted a shunt resistor in order to use the applied current as a reference signal to Lock-in amplifier. The both-end voltage of sample was differentially inputted to Lock-in amplifier, considering an influence of shunt resistor. To prevent attenuation at high frequency, short cables were used.

3. Experimental Results and Discussion

Figure 2 shows the temperature dependence of n-th-order harmonics. The amplitude and frequency of applied current are 0.02 mA and 100 Hz, respectively. Figure 2 shows data with a voltage of 5 μV or more because the measurement accuracy is lowed when the amount of harmonics is small. The odd harmonics up to 7th order appears below 200 K. This odd harmonics comes from a nonlinear conductivity. However, even harmonics are not expected to exist because it is reported that the nonlinear conductivity is reversible with the direction of current [9].

To clarify why the even harmonics response were observed, we conducted controlled experiments replacing single crystal with variable resistor. Figure 3(a) shows second harmonic as a function of fundamental harmonic of a single crystal and variable resistor. Although no harmonics are generated in principle from the pure resistor, second harmonic is observed even from a

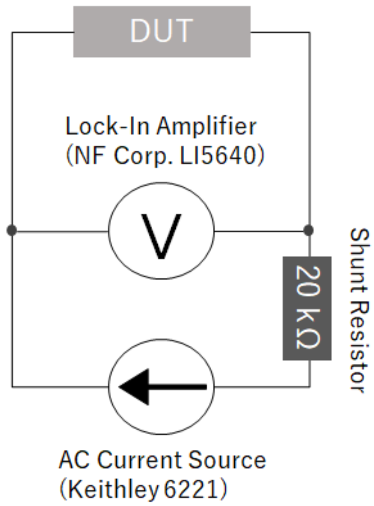

Figure 1: (Color online) Schematic of harmonic response measuring circuit. Shunt resistor (20 kΩ) is for using applied current as a reference signal to Lock-in amplifier. Both-end voltage of DUT (sample) was differentially inputted to Lock-in amplifier. To prevent attenuation at high frequency, short cables were used.

variable resistor which is a pure resistor. Possible reasons of the generation of even harmonics are a performance of low-pass filter (LPF) in Lock-in amplifier and deviation from the sine-wave of input signal due to imperfection of generator. Now, we will demonstrate how to emerge the even harmonics due to LPF in Lock-in amplifier. In a Lock-in amplifier, input signal is converted by a phase sensitive detector (PSD). Among the converted signal, components passing through a LPF are measured as is shown in Figure 3(b). An input signal including harmonics reads

$$\begin{aligned} V_s(t) &= A_{s1}\cos(\omega_s t+\theta_{s1}) + harmonics \\ &= A_{s1}\cos(\omega_s t+\theta_{s1}) + A_{s2}\cos(2\omega_s t+\theta_{s2}) + A_{s3}\cos(3\omega_s t+\theta_{s3}) + \cdots \\ &= \sum_{n=1}^{\infty} A_{sn}\cos(n\omega_s t+\theta_{sn}) \\ &= \frac{1}{2}\sum_{n=1}^{\infty} A_{sn}\left\{e^{i(n\omega_s t+\theta_{sn})} + e^{-i(n\omega_s t+\theta_{sn})}\right\} \end{aligned} \tag{1}$$

where n is the degree of harmonics, A_{sn} is the amplitude of n-th-order harmonics, ω_s is the fundamental frequency, and θ_{sn} is the phase difference be-

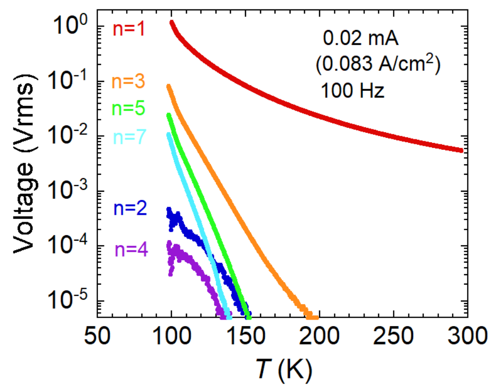

Figure 2: (Color online) Temperature dependence of n-th-order harmonics by application of sine-wave current of a single crystal of $Ca_5Ir_3O_{12}$ along the c-axis. Regarding the applied current, an amplitude is 0.02 mA (0.083 A/cm^2), and a frequency is 100 Hz, respectively.

tween a fundamental harmonic and n-th-order harmonics, respectively. The input signal is multiplied with a reference signal $V_r(t) = \sqrt{2}e^{-i\omega_r t}$ by PSD, which is given by

$$\begin{aligned} V_s(t) \cdot V_r(t) &= \frac{1}{2}\sum_{n=1}^{\infty} A_{sn}\left\{e^{i(n\omega_s t+\theta_{sn})} + e^{-i(n\omega_s t+\theta_{sn})}\right\} \cdot \sqrt{2}e^{-i\omega_r t} \\ &= \sum_{n=1}^{\infty}\left[\frac{A_{sn}}{\sqrt{2}}e^{i\{(n\omega_s-\omega_r)t+\theta_{sn}\}} + \frac{A_{sn}}{\sqrt{2}}e^{-i\{(n\omega_s+\omega_r)t+\theta_{sn}\}}\right] \end{aligned} \quad (2)$$

The converted signal is broken down into $(n\omega_s - \omega_r)$ and $(n\omega_s + \omega_r)$ terms. When $n\omega_s = \omega_r$, there is a component converted into DC, and only the DC component can ideally pass through a LPF. Therefore, a desired harmonic is obtained by voluntarily adjusting the ω_r. It is noted that ω_r is not frequency of reference signal, but the frequency of integral multiples of the frequency of reference signal.

Actually, LPF cannot completely intercept a high frequency component though LPF can attenuate it. As is shown in Fig. 3(a), second harmonic is approximately 0.1% of fundamental harmonic. Although there is a difference between a single crystal and a variable resistor in Fig. 3(a), this is considered due to a difference whether there are harmonics or not. Consequently, we can conclude that the even harmonics are not intrinsic response from a single

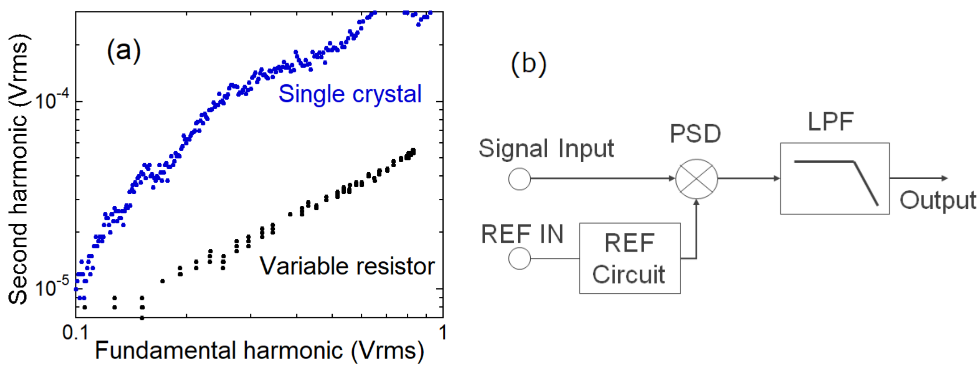

Figure 3: (Color online) (a) Second harmonic as a function of fundamental harmonic of a single crystal of $Ca_5Ir_3O_{12}$ and variable resistor. The temperature range in this figure is 100 - 150 K. For single crystal, the data from Figure 2 are used. For variable resistor, the measurements were performed at room temperature. We control the fundamental harmonic's voltage by changing a resistance of variable resistor. (b) Conceptual scheme of Lock-in amplifier. PSD stands for phase sensitive detector.

crystal of $Ca_5Ir_3O_{12}$ but due to such as a performance of LPF in Lock-in amplifier and deviation from the sine-wave of input signal.

Next, we will discuss the temperature dependence of the nonlinearity. The presence of harmonics means distortion of waveform, which is a proof of nonlinear conductivity. In short, the electrical nonlinear conductivity discovered by a pulse current method was also observed by application of AC current. In addition, this nonlinear conductivity exists even in application of current close to zero. As is shown in Fig. 2, there is a clear trend of increasing fundamental and odd harmonics on cooling. Therefore, we found that the nonlinearity increases with decreasing temperature.

To more quantitatively evaluate the nonlinearity, a resistance normalized with a resistance at zero current limit was used. The resistance R and the limit R_0 are obtained by dividing amplitude of a voltage response (V_{amp}) and a sine-wave tangent to a voltage response when $\omega t = 0$ (A) by amplitude of applied current (I), respectively. The voltage response from a single crystal by application of sine-wave current is given by

$$V_{\mathrm{resp}} = V_1 \sin \omega t + V_3 \sin(3\omega t + \theta_3) + V_5 \sin(5\omega t + \theta_5) + V_7 \sin(7\omega t + \theta_7). \quad (3)$$

Thus, amplitude of the voltage response is

$$V_{\mathrm{amp}} = V_1 - V_3 \cos \theta_3 + V_5 \cos \theta_5 - V_7 \cos \theta_7 \quad (4)$$

By defining the sine-wave tangent to the voltage response when $\omega t = 0$ as $V = A\sin(\omega t)$, the amplitude of the sine-wave is

$$A = V_1 + 3V_3\cos\theta_3 + 5V_5\cos\theta_5 + 7V_7\cos\theta_7. \tag{5}$$

By using Equations (4) and (5), $R = V_{amp}/I$ and $R_0 = A/I$ were calculated, respectively.

Figure 4(a) shows temperature dependence of R_0. As is shown in Fig. 4(a), R_0 is approximately consistent regardless of amplitude of applied current. Figure 4(b) shows the temperature dependence of the resistance normalized with the limit as current approaches zero of the resistance (R/R_0). The normalized resistance decreases with decreasing temperature. Decreasing the normalized resistance means increasing the nonlinearity; therefore the nonlinearity increases with decreasing temperature. From Fig. 4(b), there is markedly nonlinearity above two transition temperature, 7.8 K and 105 K.

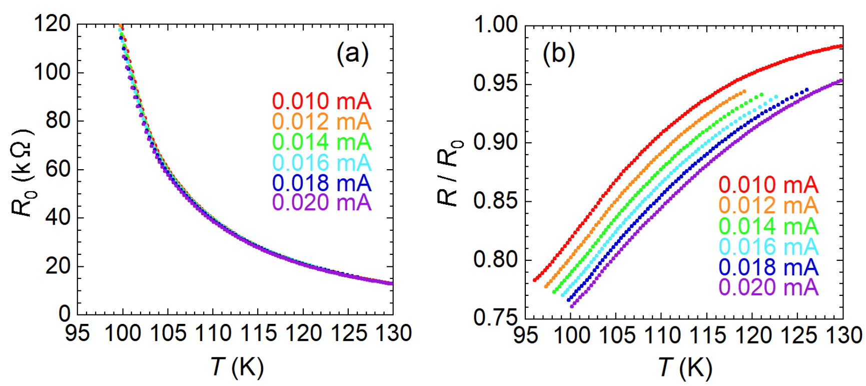

Figure 4: (Color online) (a) Temperature dependence of the resistance at zero current limit (R_0). (b) Temperature dependence of resistance normalized with R_0.

Figure 5 shows $\ln R_0$ vs $(1/T)^x$ with three different x values ($x = 1, 2/3, 1/2$), in a temperature range of 120 to 300 K. The black solid lines in Figure 5 are fits to

$$\ln R_0 = \ln R_1 + \left(\frac{T_0}{T}\right)^x \tag{6}$$

where R_1 and T_0 are fitting parameters. In general, the exponent x is 1/4, 1/2, or 1 corresponding to 3D Mott variable range hopping (VRH), 1D Mott or Efros-Shklovskii (ES) VRH, and nearest neighbor hopping (NNH), respectively [18]. From Fig. 5, it is clear that $x = 2/3$ is the most acceptable fit to the data, in spite of previously reported result that an electric conductivity of $Ca_5Ir_3O_{12}$ along the c-axis obeys 1D Mott or ES VRH ($x = 1/2$) [9]. The exponent $x = 2/3$ has also reported in ZnO [18] and Au nanocrystals [19]. This can be explained by an adaptation of the ES VRH model that replaced the conventionally used Miller-Abrahams expression for nonresonant transfer by an expression which is based on temporal energy fluctuations [18]. In addition, the exponent $x = 2/3$ is explained by Fogler, Teber and Shklovskii (FTS) VRH theory [20]. According to the FTS VRH, the exponent x can be expressed by

$$x = \frac{\mu + 1}{\mu + d + 1} \tag{7}$$

where d is the dimensionality of the array of the 1D rods and μ is the exponent of a power-law density of state $g(\epsilon) \propto \epsilon^{\mu}$ [21]. Although it is not clear which VRH model can explain the conductivity of a single crystal of $Ca_5Ir_3O_{12}$, it is clear that a mechanism of the electrical conduction is VRH. The notable aspect of hopping conduction is the field assisted motion of charge carriers between localized states [22]. In other words, an electrical resistance is dependence on an electric field. [23]. It can therefore be assumed that the nonlinear electrical conductivity is due to the electric field-assisted.

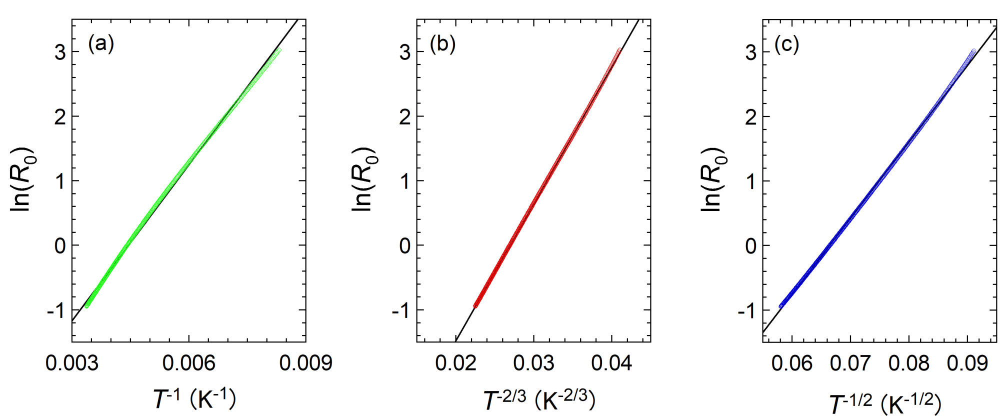

Figure 5: (Color online) ln R_0 plotted on different temperature scales: (a) T^{-1}, (b) $T^{-\frac{1}{2}}$ and (c) $T^{-\frac{2}{3}}$.

4. Summary

In this study, we have carried out harmonic voltage response by application of sine-wave current to a single crystal of $Ca_5Ir_3O_{12}$ along the c-axis to clarify the detail of the nonlinear electrical conductivity of the geometrically frustrated iridate $Ca_5Ir_3O_{12}$. This study has shown that the nonlinear conductivity exists even in application of current close to zero, and in the non-ordered state above their transition temperatures. In addition, temperature dependence of the resistance estimated at the zero current limit shows $\ln R_0 \propto T^{-2/3}$, which can be explained by an adaptation of ES VRH or FTS VRH model. From this analysis result, the nonlinear conductivity comes form the field-assisted hopping conduction.

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