

# Strongly correlated electrons in ferroelectric metal $\text{LiOsO}_3$

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## Abstract

The metallic  $\text{LiOsO}_3$  undergoes a transition to a polar phase below  $T_s \approx 140$  K. This unusual property provides a unique opportunity to study the interaction between free electrons and electric dipoles. We report a suite of measurements of physical properties in  $\text{LiOsO}_3$  as a function of temperature, including resistivity and magnetoresistance on single crystal samples down to 0.16 K, thermoelectric power, high-precision magnetization, specific heat, and thermal conductivity on textured single crystal samples. Enhancements from the electron contribution to the specific heat and the paramagnetic susceptibility indicate that electrons in  $\text{LiOsO}_3$  are highly correlated. **An anomalously large Kadowaki-Woods ratio also supports the argument of strongly correlated electrons in  $\text{LiOsO}_3$ .** In the non-polar phase above  $T_s$ , electrons are coupled strongly to the lattice vibrations, which leads to the resistivity saturation at high temperatures and eventually the crossover to the hopping conduction. The data of thermal conductivity and specific heat are consistent with an order-disorder transition at  $T_s$ . The analysis of critical behavior in the resistivity, specific heat, and the thermal conductivity provides useful information for understanding the electron-dipole interaction in  $\text{LiOsO}_3$ .

## I. Introduction

Almost all ferroelectrics are insulators. Ferroelectricity arises due to the long-range dipole-dipole interaction.<sup>1</sup> Metallicity and ferroelectricity are seemingly incompatible since free electrons screen the dipole-dipole interaction. The transition to a polar phase is possible in a metal as long as free electrons do not interact strongly with the transverse optical phonons. This possibility was first postulated by Anderson and Blount when they studied the martensite transition in  $V_3Si$  in 1965.<sup>2</sup> The discovery of polar metal  $LiOsO_3$ <sup>3</sup> revived the interest on this subject. It has been recognized that  $LiOsO_3$  fulfills the definition of a ferroelectric metal given by Anderson and Blount.<sup>4</sup> The possible interplay among the electron-dipole interaction, electron-phonon interaction, Hund's coupling, spin-orbit coupling, and electron-electron interaction in  $LiOsO_3$  also triggered computational and theoretical studies.<sup>5 6 7 8 9 10 11</sup> However, it is still controversial on issues such whether electron-phonon interaction is weak in  $LiOsO_3$ , which allows the ferroelectric transition as proposed by Anderson and Blount; whether  $LiOsO_3$  is a strongly correlated system, and whether the non-polar to polar transition alters the band structure for the states near the Fermi energy.  $LiOsO_3$  is a metal from 300 K to 2 K. At low temperatures, the  $\rho(T)$  exhibits a power law dependence and the residual resistivity is significantly large. The polar to non-polar transition at  $T_s=140$  K leads to a sign change of the curvature in  $\rho(T)$ ; the resistivity saturates quickly for  $T > T_s$ .<sup>3</sup> The Raman study on a  $LiOsO_3$  crystal verified a second-order phase transition at  $T_s$ .<sup>12</sup> By tracking down a Raman active mode  $^3E_g$ , Jin et al. were able to extract important information about dynamics of the  $A_{2u}$  mode associated with Li displacement near  $T_s$  and the critical behavior at the transition.<sup>13</sup> The data allow them to derive a strong electron phonon coupling which seems contradictory to the assumption made by Anderson and Blount for a ferroelectric metal. In the same report, the authors have measured Hall coefficient. The data indicate an anisotropic scattering that increases, especially at  $T < T_s$ , with decreasing temperature. In contrast, a study with THz pump-probe on  $LiOsO_3$  concluded that the itinerant electrons are decoupled from the soft transverse optical phonons.<sup>14</sup> The Raman study indicates negligible critical fluctuations in the vicinity of nonpolar to polar transition. This observation appears to be inconsistent with the conclusion from an optical study with second-harmonic generation (SHG).<sup>15</sup>  $LiOsO_3$  is a bad metal as characterized by infrared spectroscopy, which shows a small quasiparticle spectral weight in the energy range from the Drude analysis, a clear sign for being close to a Mott-Hubbard transition.<sup>16</sup> However, there are no clear signatures for a strongly correlated system from the reported results of transport and magnetic properties of  $LiOsO_3$ . Moreover, whether  $LiOsO_3$  can become superconducting at low temperatures as predicted by Anderson and Blount for a ferroelectric metal remains unclear.<sup>2</sup> The non-polar to polar phase transition in  $LiOsO_3$  changes the phonon structure. It remains unknown how the phonon structural change influences the thermal transport property. A careful comparative study between  $LiOsO_3$  and other ferroelectric metals has not been made. This study aims to address these questions.

In comparison with the electron-electron interactions, electron-phonon interactions, and electron-magnon interactions, the interaction between free electrons and dipoles has been rarely studied since few ferroelectric systems are conducting. In the conductor  $\text{Pb}_{1-x}\text{Ge}_x\text{Te}$ , the off-center Ge ion form an electric dipole that interacts with free electrons. The two-level system model developed by Katayama *et al.*<sup>17</sup> can account for the anomalous logarithmic increase of resistivity at low temperatures. The presence of free electrons in turn influences the dipole-dipole interaction  $V_{dd}$ , *i.e.* making the  $V_{dd}$  having alternating sign as a function of  $R$  (the distance between dipoles) similar to the RKKY interaction. The tendency of having free electrons in dipole systems is to promote the dipole glass state instead of a long-range ordering.<sup>18</sup>

$\text{SrTiO}_3$  is well-known for quantum ferroelectric **since it is at the tipping point for a ferroelectric transition**.<sup>19</sup> The cubic perovskite exhibits a ferroelectric transition for the  $^{18}\text{O}$  enriched sample. Ferroelectricity can also be induced in a very narrow range ( $0.0018 < x < 0.02$ ) of the Ca doping in  $\text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3$ . The ferroelectric transition survives in the metallic phase  $\text{Sr}_{1-x}\text{Ca}_x\text{TiO}_{3-\delta}$  with oxygen deficiencies.<sup>20</sup> As in  $\text{Pb}_{1-x}\text{Ge}_x\text{Te}$ , the ferroelectric transition triggers a resistivity upturn in  $\text{Sr}_{1-x}\text{Ca}_x\text{TiO}_{3-\delta}$ . The authors adopted the same dipole version of the RKKY interaction to account for the resistivity anomaly.

The ferroelectric metal (with the definition by Anderson and Blount<sup>2</sup>)  $\text{LiOsO}_3$  is dramatically different from the systems above. (1) The density of off-center ions, *i.e.* the density of dipoles, is extremely low in  $\text{Pb}_{1-x}\text{Ge}_x\text{Te}$  and  $\text{Sr}_{1-x}\text{Ca}_x\text{TiO}_{3-\delta}$  in comparison with that in  $\text{LiOsO}_3$ . (2) On cooling, the ferroelectric transition triggers a drop of resistivity in  $\text{LiOsO}_3$  instead of an upturn in  $\text{Pb}_{1-x}\text{Ge}_x\text{Te}$  and  $\text{Sr}_{1-x}\text{Ca}_x\text{TiO}_{3-\delta}$ . (3)  $\text{LiOsO}_3$  is not a regular metal as seen from the resistivity saturation above  $T_s$ . (4) The interaction between free electrons and dipoles appears to enhance the long-range dipole ordering. (5) Most importantly, electrons in  $\text{LiOsO}_3$  are strongly correlated as demonstrated in this work. How to treat the interplay between electron-electron interactions and electron-dipole interaction is a new topic in condensed matter physics;  $\text{LiOsO}_3$  is a unique system for the study.

## II. Transport properties

The samples in this study were synthesized under high pressure in Japan and in the US. The detail of high-pressure synthesis can be found in a previous report.<sup>3</sup> **Osmium metal is stable in dry air. However,  $\text{OsO}_2$  may react with oxygen in air to form very toxic  $\text{OsO}_4$ . All the high-pressure assemblies were prepared in the glovebox with pure Ar (with  $\text{O}_2$  in 0.1 ppm). The high-pressure product  $\text{LiOsO}_3$  with  $\text{Os}^{5+}$  is stable in air as checked over the time with X-ray powder diffraction.** Measurements of resistivity  $\rho(T)$  were made on needle shape crystals with a  $\sim 150$   $\mu\text{m}$  length and a 20-30  $\mu\text{m}$  cross section, which are not oriented. Measurements of the thermoelectric power were made on pellets consisting of textured crystals with both the thermal transport option in a Physical Property Measurement System (PPMS) from Quantum Design and a home-made system. Several pieces of crystals from two batches of high-pressure synthesis

were measured. Essential features of  $\rho(T)$  and  $S(T)$  are highly reproducible and the residual resistivity values in these crystals fall in a narrow range. Some crystals show a loop of  $\rho(T)$  around  $T_s$  between the cooling down and warming up runs, which can be attributed to the crystal crack at the domain boundaries during the thermal cycles. These loops have never been observed in  $S(T)$ , **which confirms the grain boundary effects in origin**. In comparison with the resistivity data reported previously,<sup>3</sup> the resistivity measurement in this study was made over a much wider temperature range 0.16 -360 K. Moreover, the residual resistivity of crystals from two different batches of  $\text{LiOsO}_3$  is generally smaller than that in the reported data.<sup>3</sup>

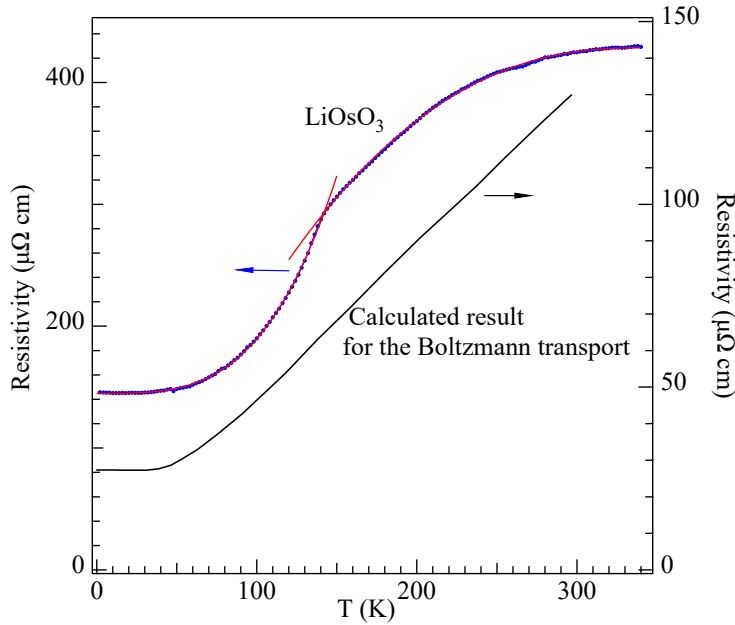


Fig.1 Temperature dependence of resistivity of  $\text{LiOsO}_3$  crystal. Lines in the plot are from the fitting to power laws, see the text for details. The resistivity data with scale on the right side of vertical axis are from the calculation in studying the transport property of  $\text{SrRuO}_3$ .<sup>21</sup> **The calculated result is used to show the typical behavior of a metal that can be accounted for by the Boltzmann model.**

Fig.1 displays a typical result of  $\rho(T)$  measured on the  $\text{LiOsO}_3$  crystal. The transition to a polar phase on cooling through  $T_s$  causes an abrupt drop of resistivity. The  $\rho(T)$  in both the non-polar phase and the polar phase is far from our understanding for a regular metal. For a regular metal, the temperature dependence of resistivity can be described by the Boltzmann gas model with the electron-phonon interaction; examples of regular metals include  $\text{ReO}_3$ ,  $\text{BaPbO}_3$ ,  $\text{CoSi}$ , and  $\text{Pd}_2\text{Si}$ .<sup>22</sup> A Bloch-Grüneisen curve of the resistivity in studying  $\text{SrRuO}_3$  is superimposed in Fig.1, which is roughly a power law  $\rho \sim T^5$  at low temperatures and a linear relationship  $\rho \sim T$  at high temperatures. These features can be found in the metals listed above but appear to be missed in the  $\rho(T)$  of  $\text{LiOsO}_3$ . The residual resistivity  $\rho_0$  of  $\text{LiOsO}_3$  is unusually high. The  $\rho(T)$  for the entire temperature range in this study can be fit to the power laws  $\rho \sim T^{3.4}$  for  $T < T_s$  and  $\rho \sim (340-T)^{2.37}$  for  $T > T_s$ . The resistivity measurement on two  $\text{LiOsO}_3$  single crystals were made

down to 160 mK with a dilution refrigerator in the PPMS; the results are identical and the  $\rho(T)$  of one crystal is shown in Fig.2. Results shown in Fig.1 and Fig.2 were measured on different crystals; the offset of the resistivity at 2 K between the results in Fig.1 and Fig.2 can be attributed to the measurement uncertainty of the sample's dimension and the distance between voltage leads. The abrupt drop of the resistivity at  $T \approx 0.2$  K appears to be related to a superconducting transition of Os metal<sup>23</sup> since high resolution synchrotron powder diffraction on the powder sample made by pulverizing the crystal reveals a small amount of Os metal phase. The filamentary Os metal phase does not establish a percolation connection through the crystal. Therefore,  $\rho(T)$  only shows a small drop at the superconducting transition temperature of Os metal. The superconducting origin of the resistivity anomaly is further confirmed by the measurement with a magnetic field  $H=9$  T. The resistivity anomaly together with an obvious resistivity reduction in the vicinity of sub Kelvin due to pairing fluctuations is fully removed under  $H=9$  T. A small MR effect at  $T > 0.2$  K is understandable based on the Kohler's rule for a metal. We have fit  $\rho(T)$  at 9 Tesla to a power law  $\rho(T) = \rho_0 + AT^n$  with  $n = 1.98 \pm 0.26$ . The effect of electron-phonon interactions is much smaller than electron-electron interactions at low temperatures. The fitting parameter  $n \approx 2$  indicates a Landau-Fermi liquid behavior in the polar phase of  $\text{LiOsO}_3$  at low temperatures. Another fitting parameter  $A$  will be used for the Kadowaki-Woods ratio that is discussed with the specific heat result.

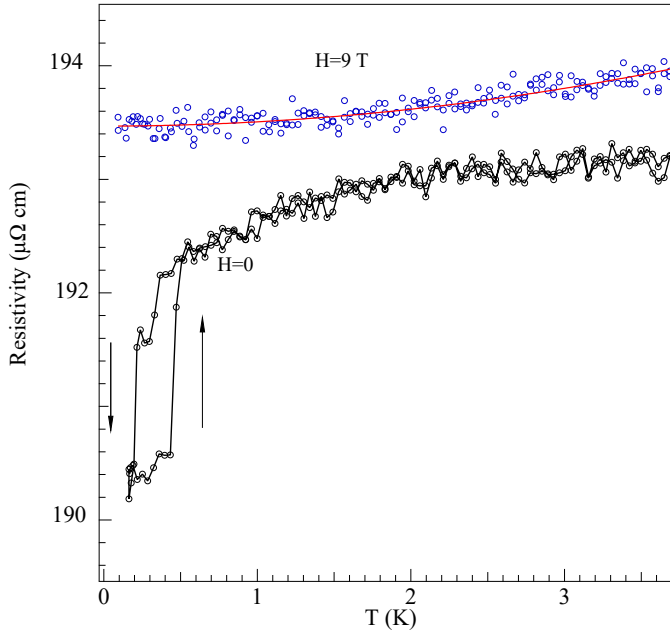


Fig.2 Temperature dependence of resistivity for  $\text{LiOsO}_3$  crystal at low temperatures. The line in  $\rho(T)$  under 9 Tesla is the fitting result to a power law  $\rho(T) = \rho_0 + AT^n$ , see the text for the discussion about the fitting result.

It should be noticed that  $\text{LiOsO}_3$  shows an unusually high residual resistivity  $\rho_0$  obtained by extrapolating the  $\rho(T)$  at 9 T to zero K, in which the resistivity change due to any filamentary superconductivity is removed. Electric resistivity in a metal is caused by electrons interacting with lattice vibrations and defects. Thermal vibrations scatter electrons, which can be treated with the Boltzmann gas model. At zero K, the resistivity comes from scattering on defects. A large residual resistivity may be the intrinsic property of the oxide. Li ions are at 6a position (0,0,z) and (0,0,z+1/2) in the  $\text{LiNbO}_3$  structure with the space group  $R3c$ . The ferroelectric displacement originates from Li moving along the z axis. The thermal displacement factor  $\beta_{33}$  for the Li site increases drastically on cooling through  $T_s$  and remains large to the lowest temperature.<sup>3</sup> A larger thermal displacement factor at low temperatures indicates some randomness of Li displacement along the z direction, which contributes the scattering to free electrons and should be the primary source for a large residual resistivity.

Whereas the curvature of  $\rho(T)$  at  $T < T_s$  is the same as the prediction from the Boltzmann gas model, the power-law dependence  $\rho \sim T^{3.4}$  to 140 K differentiates  $\text{LiOsO}_3$  from a regular metal.  $T_s$  marks a sign change of the curvature of  $\rho(T)$ , which results in a resistivity saturation at  $T > T_s$ . With a partially filled  $t_{2g}$  orbital in the low spin  $\text{Os}^{5+}$ ,  $\text{LiOsO}_3$  could be a good candidate of Hund's metal. In a Hund's metal, electron hopping between atoms has the penalty of  $J_H$  if the spin state at the receiving atom violates the Hund's rule in addition to the on-site Coulomb energy.<sup>24</sup> Mixing of  $J_H$  into a strongly correlated system leads to a distinct feature in resistivity. The theory predicts a characteristic temperature  $T^*$  which is proportional to the Drude weight in a metallic system.  $T^*$  separates a coherent state at low temperature described by the Fermi liquid state and incoherent state at high temperatures which shows a  $\rho(T)$  with impending saturation as temperature increases.<sup>24</sup> The resistivity of iron pnictide  $\text{KFe}_2\text{As}_2$  fits the description of a Hund's metal well.<sup>25</sup> Back to  $\text{LiOsO}_3$ , the remarkable sign change of the curvature at  $T_s$  may suggest the transition at  $T_s$  coincides with a coherence-incoherence crossover as in a Hund's metal. **A recent theoretical work has shown that the electronic state in  $\text{LiOsO}_3$  is close to a Hund's-Mott insulator transition and predicted a crossover from a metallic to an incoherent behavior.**<sup>10</sup>

On the other hand, the  $\rho(T)$  of  $\text{LiOsO}_3$  at high temperatures resembles the resistivity saturation found in A15 compound.<sup>26</sup> Theories to rationalize this behavior evolved over time. The early model states that resistivity deviates from the prediction of the gas model as the electron mean free path is close to the lattice parameter. A more convincing model to describe the phenomena is that the electron-phonon interaction is so strong that the Migdal approximation, one of the key requisitions to make the gas model work, is no longer valid.<sup>27</sup> The resistivity saturation is the sign of a smooth crossover from electron scattering to electron hopping. This scenario appears to fit the case of  $\text{LiOsO}_3$ . We have indeed observed a resistivity decrease with increasing temperature at  $T > 360$  K (not shown in Fig.1). A strong electron-phonon interaction based on the scenario above is consistent with the conclusion from Raman study on  $\text{LiOsO}_3$ ;<sup>13</sup> the study also gives a microscopic picture of how electrons couple with dipoles. The crossover from electron scattering to electron hopping at high temperatures and the conclusion from the Raman

study in  $\text{LiOsO}_3$ <sup>13</sup> are inconsistent with the mechanism of ferroelectric metal by Anderson and Blount, which is based on a weak electron-transverse phonon coupling. The real driving force for the transition to a polar phase in  $\text{LiOsO}_3$  deserves further studies. A drastic increase of  $T_s$  under pressure<sup>28 29</sup> and the corresponding change in the structure<sup>29</sup> indicate that the local structural instability may be the driving force for the transition to a polar phase at  $T_s$ .

Fig.3 displays the result of thermoelectric power  $S$ ; it is highly repeatable on several textured  $\text{LiOsO}_3$  crystals. The overall negative  $S$  indicates that  $\text{LiOsO}_3$  is an electronic conductor which is consistent with the Hall measurement.<sup>13</sup> A broad maximum of  $|S|$  occurs at 200 K followed by a nearly linear decrease of  $|S|$  as temperature approaches to zero K. In the measurement for testing the magnetic field dependence of the thermoelectric power, the contribution from the Nernst effect has been ruled out since resulting  $S(T)$  with  $\pm H$  are overlapped. The magnitude of  $S$  is slightly suppressed under magnetic field  $H=1$  T in the temperature range  $100 < T < 220$  K and no field dependence is found for  $H > 1$  T (up to 9T) in comparison with  $S$  at  $H=1$  T;  $S(T)$  for  $H=9$  T is shown in Fig.3.

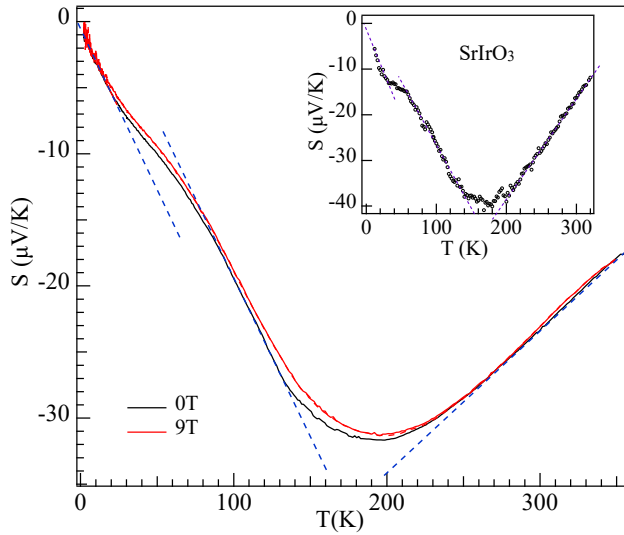


Fig.3 Temperature dependence of the thermoelectric power for  $\text{LiOsO}_3$ ; lines inside the plot are guides to eyes. Inset: temperature dependence of the thermoelectric power for perovskite  $\text{SrIrO}_3$ .<sup>30</sup>  $\text{SrIrO}_3$  also shows an anomalous thermoelectric power, *i.e.* a hump (of magnitude) near 180 K, which is stunningly similar to the  $S(T)$  of  $\text{LiOsO}_3$ .

The thermoelectric power in a metal can be treated roughly as the electronic contribution to specific heat per electron, *i.e.*  $S \approx C_e/e = (\gamma/e)T$  which provides a good explanation of the linear decrease of  $|S|$  in  $\text{LiOsO}_3$  as  $T$  approaches zero K. Electrons are scattered by impurities and lattice vibrations in a solid. In the temperature range  $T \geq \theta$  or  $T \ll \theta$ ,  $\theta$  is the Debye temperature, the thermoelectric power is dominated by electron-impurities scattering. In this case,  $S$  can be



expressed by the diffusive formula  $S = (\frac{\pi^2 k^2}{e E_F}) T$  for  $T \ll \theta$ .<sup>31</sup> Taking  $E_F \approx 2\text{eV}$  from the band calculation for  $\text{LiOsO}_3$ ,<sup>3</sup>  $S = -0.037 T$  ( $\mu\text{V/K}$ ) is obtained; the absolute value of the slope  $0.037 \mu\text{V/K}^2$  is much smaller than  $0.23 \mu\text{V/K}^2$  obtained by fitting the  $S(T)$  at  $T < 25 \text{ K}$  in Fig.3. The diffuse formula  $S = (\frac{\pi^2 k^2}{e E_F}) T$  is derived on an assumption of a sphere Fermi surface. The ferroelectric  $\text{LiOsO}_3$  must have a much more distorted Fermi surface. A general expression of  $S$  is needed in order to understand the profile of  $S$  with the  $E_F$  at different locations in a band,

$$S = \frac{1}{eT} \int (E - E_F) \sigma(E) \frac{\partial f_0}{\partial E} dE / \int \sigma(E) \frac{\partial f_0}{\partial E} dE, \quad (1)$$

where  $\sigma(E)$  is defined by  $\sigma = \int \sigma(E) dE$ , and  $f_0$  is the Fermi-Dirac distribution function. The thermoelectric power is a measure of the asymmetry of the energy dependence conductivity crossing the Fermi energy. For a single band system, a large  $|S|$  is expected to occur for the  $E_F$  located in top or bottom of the band. **Both  $\text{LiOsO}_3$  and  $\text{NaOsO}_3$  have the  $t_{2g}^3$  electronic configuration. These systems with the Fermi energy located in the middle of the  $\pi^*$  band consisting of highly hybridized O:2p and Os:5d orbitals are expected to exhibit a small and weak temperature-dependent  $S$ .  $S(T)$  of  $\text{NaOsO}_3$  (unpublished) at temperatures above the metal-insulator transition fulfills this expectation.** A large  $|S|$  of  $\text{LiOsO}_3$  can be attributed to the peculiar electron density of state (DOS) in the  $R3c$  structure. A pronounced minimum below  $E_F$  within  $0.5 \text{ eV}$ <sup>3</sup> makes effectively the  $E_F$  of  $\text{LiOsO}_3$  at the bottom of a band, which gives rise to a negative  $S$  with a large magnitude in  $\text{LiOsO}_3$ .

In a typical broad-band metal like copper, the electron-phonon interaction manifests as the phonon-drag effect in the thermoelectric power, which is normally present as a broad hump in  $S$  at  $T \sim \theta/4$ ,  $\theta$  is the Debye temperature.<sup>31</sup> The physics of phonon-drag effect is that in addition to the electron diffusing driven by the temperature gradient the travel of phonons with a long mean-free path adds a driving force on electrons; so that the drag effect would have the temperature dependence of  $1/T$ . At low temperatures, a fast reduction of the phonon population makes the effect vanishing in  $T^3$ . Therefore, the phonon-drag effect essentially resembles the temperature dependence of phonon thermal conductivity. Given a  $\theta$  in a range 155-675K depending on temperature from the specific-heat measurement and a broad peak in the thermal conductivity discussed in a following section, a hump in  $S(T)$  at 30 K is expected. Whereas  $S(T)$  of  $\text{LiOsO}_3$  in Fig.3 deviates from a linear behavior around 30 K, the essential feature of a typical phonon-drag effect is missing here. In a narrow band system, an enhanced electron-phonon coupling reduces significantly the phonon mean free path. As a result, the phonon-drag effect is suppressed. A good example can be found in  $\text{La}_{1-x}\text{Nd}_x\text{CuO}_3$ .<sup>32</sup> The bandwidth is progressively reduced as increasing of the Nd substitution which bends the Cu-O-Cu bond angle from 180 degree in this rhombohedral perovskite structure. The phonon-drag effect found in  $\text{LaCuO}_3$  is gradually reduced and vanishes as  $x$  increases in  $\text{La}_{1-x}\text{Nd}_x\text{CuO}_3$ . Missing the phonon-drag effect in  $\text{LiOsO}_3$



signals strongly correlated electrons. We will come back to this point when we discuss the data of specific heat and magnetic susceptibility.

Another important feature in  $S(T)$  of  $\text{LiOsO}_3$  is that  $T_s$  separates a roughly linear temperature dependence  $S \sim T$  in the polar phase at  $T < T_s$  from a highly unusual  $S(T)$  in the non-polar phase at  $T > T_s$ . While much enhanced, the linear temperature dependence of  $S(T)$  at  $0 < T < 25$  K and  $70 < T < 140$  K and the monotonic increase of  $|S|$  with increasing temperature at  $25 < T < 70$  K in the polar phase is consistent with the diffusive thermoelectric power, *i.e.*  $S \sim T$ . A broad hump of  $|S|$  near 200 K is unusual for a metal, but have been observed in other strongly correlated systems such as the single-layer, hole-doped cuprate superconductor<sup>33</sup> and perovskite  $\text{SrIrO}_3$ .<sup>30</sup> As displayed in the inset of Fig.3,  $S(T)$  of  $\text{SrIrO}_3$  is stunningly similar to that of  $\text{LiOsO}_3$ .

Although there is no a good understanding about the broad hump in  $S(T)$  at high temperatures, it is interesting to note that the phonon-drag effect is missed in the strongly correlated systems if there is a hump in  $S(T)$  at high temperatures. The doping of non-magnetic  $\text{Sn}^{4+}$  in  $\text{SrIr}_{1-x}\text{Sn}_x\text{O}_3$  leads to a ferromagnetic insulator, which implies that  $\text{SrIrO}_3$  is at the crossover of itinerant and localized electronic behavior. Although there is no obvious hump of  $S(T)$  of  $\text{LaCuO}_3$  and  $\text{LaNiO}_3$  at high temperatures,<sup>34</sup> strong correlations as identified by the enhancements of  $\gamma$  and  $\chi_0$  is related to a much reduced phonon-drag effect. However, the phonon-drag effect is restored under high pressure in these two narrow band systems.<sup>32</sup> Another general feature for the systems having the  $S(T)$  with a broad hump at high temperatures is that the coefficient  $A$  in  $S = \pm AT$  as  $T$  approaches zero K is much larger than that the diffusive formula can predict, for example,  $A_{\text{measured}} = 0.23 \mu\text{V}/\text{K}^2$  versus  $A_{\text{predicted}} = 0.037 \mu\text{V}/\text{K}^2$  for  $\text{LiOsO}_3$ . The enhanced  $A$  is caused by the complex Fermi surface in the crystal. The Boltzmann-gas model can give rise to a  $S = \pm AT$  at  $T \ll \theta$  and  $T > \theta$ , but the coefficient  $A$  at high temperatures is only 1/3 of that at low temperatures.<sup>31</sup> Therefore, the broad hump at 200 K in  $\text{LiOsO}_3$  may be a part of the crossover between the low temperature  $S = -AT$  and the high-temperature  $S = -(A/3)T$  at  $T > 400$  K or even higher temperatures. In summary, while increasing the slope in the diffusive formula of thermoelectric  $S = \pm AT$  at low temperatures, strong electron correlations suppresses the phonon-drag effect, but lead to a broad hump of the thermoelectric power at high temperatures in metals.

$S(T)$  of  $\text{LiOsO}_3$  becomes field-dependent in a narrow range near  $T_s$ . Magnetic field suppresses  $|S|$ , which occurs mainly at  $H < 1$  T; almost no field dependence is found for  $H > 1$  T. The field dependence provides useful information to understand how the electron-impurity scattering and electron-phonon interaction contribute to the thermoelectric power. Hasegawa *et al.*<sup>35</sup> have modeled the magneto-Seebeck coefficient of Bismuth. They found a larger magneto-Seebeck coefficient if the electron-acoustic phonon scattering is dominant; the magneto-Seebeck coefficient becomes negligible in the case of electron-impurity scattering. A very small to negligible field effect on  $S$  in  $\text{LiOsO}_3$  over the entire temperature range studied suggests that electron-impurity scattering is dominant in the thermoelectric power, which is consistent with the analysis of  $S(T)$  based on the diffusive formula above. However, critical fluctuations of the polar

phonon mode as revealed by the SHG experiment<sup>15</sup> may contribute to a small magneto-Seebeck effect near  $T_s$ .

### III. Specific heat and the critical phenomena

Fig.4 displays the result of specific-heat  $C_p$  measurement on the  $\text{LiOsO}_3$  sample. The transition to the polar phase at  $T_s$  creates a clear  $\lambda$ -shape anomaly in  $C_p$ . By excluding the  $C_p$  data at temperatures in the vicinity of the phase transition, the lattice contribution to  $C_p$  can be fit well to a Debye-Einstein model as shown in Fig.4(a). The  $\Delta C_p$  due to the phase transition can be obtained by subtracting the lattice contribution from  $C_p$ . The small anomaly near room temperature is from the puck and the grease used in the  $C_p$  measurement. The entropy change associated with the phase transition in Fig.4(b) is calculated by  $\Delta S = \int \frac{\Delta C_p}{T} dT = 3.5 \text{ J/(mol K)} = 0.42R$  which is higher than  $0.33R$  in the early report.<sup>3</sup> This discrepancy may be due to the use of a polynomial function in fitting the lattice contribution in the early report. In the plot of  $C_p/T$  versus  $T^2$  of Fig.4(c), the temperature dependence at  $5.5 < T < 12 \text{ K}$  can be fit linearly. The fitting gives a  $\gamma = 7.72 \text{ mJ/(mol K}^2\text{)}$  which is the same as that in the early report.<sup>3</sup> However, the  $\gamma_0 = 6.8 \text{ mJ/(mol K}^2\text{)}$  calculated in the early report is wrong. The authors used the unit of states/cell of DOS at the Fermi energy in their calculation. The correct unit for the DOS in the calculation is states/(eV f.u.) which gives the  $\gamma_0 = 2.6 \text{ mJ/(mol K}^2\text{)}$ . A large ratio of  $\gamma/\gamma_0$  is the first evidence for strongly correlated electrons in  $\text{LiOsO}_3$ , which is consistent with the enhancement of paramagnetic susceptibility and an antiferromagnetic ordering at  $T_N$ . The low temperature hump in the plot of  $C_p/T$  versus  $T^2$  can well be correlated with the magnetic ordering in  $\text{LiOsO}_3$ . In addition, the Kadowaki-Woods ratio  $A/\gamma^2$ ,<sup>36</sup>  $A$  is the parameter in fitting  $\rho(T)$  to the Fermi liquid behavior  $\rho(T) = \rho_0 + AT^2$ , provides information about electron correlations in a metallic system. Comparing with a  $A/\gamma^2 \approx 0.4 \mu\Omega \text{ cm mol}^2\text{K}^2\text{J}^{-2}$  found for regular metals, a much-enhanced  $A/\gamma^2 \approx 89 \mu\Omega \text{ cm mol}^2\text{K}^2\text{J}^{-2}$  obtained for  $\text{LiOsO}_3$  suggests strong correlated electrons. Although for a group of materials including strongly correlated electronic systems, a unified Kadowaki-Woods ratio can derived by adding a material-specific parameter  $A/(\gamma^2 f_{dx})$ ,<sup>37</sup> a comparison of  $A/\gamma^2$  is still a simplest way to identify the strongly correlated electronic systems.

The critical behavior near the phase transition in the plot of  $\Delta C_p = C_{\text{dipole}}$  versus the reduced temperature  $t = (T - T_c)/T_c$  in Fig.4(d) has been analyzed with the formula of conventional theory  $C_{\text{mag}} = (A_{\pm}/\alpha)|t|^{-\alpha}(1 + D_{\pm}|t|^{0.5}) + S_0 + S_1 t$ . An  $\alpha = 0.11$  from the fitting makes the phase transition to a polar phase similar to a magnetic transition with 3D Ising interaction. However, the ratio  $A^+/A^- = 1.2$  is significantly larger than the prediction of 3D Ising model. These data will be useful to test any theories of critical behavior for the ferroelectric transition, especially the ferroelectric transition in a metal. In contrast, by analyzing the Raman data on  $^3E_g$  mode which is coupled to the polar mode, Jin *et al.*<sup>13</sup> obtained a mean-field behavior at the phase transition. Moreover, the authors obtained a Weiss constant  $\theta < T_s$  by fitting the dielectric susceptibility to a Curie-Weiss law. It is highly unusual that a Weiss constant is lower than the transition temperature for either a ferromagnetic or a ferroelectric transition. The absence of critical fluctuations and a reduced

Weiss constant in the Raman study have been attributed to the screening effect on the long-range dipole-dipole interaction.<sup>13</sup> Critical fluctuations near  $T_s$  found from the specific heat in this study makes the method used in the Raman study questionable. The dielectric susceptibility in the paraelectric phase is derived from the line width of  $^3E_g$  mode. This method appears not suitable for the study of critical behavior. Moreover, it is incorrect to say that the presence of itinerant electrons lowers the Weiss constant but not the transition temperature  $T_s$ . **Critical fluctuations derived from the specific heat study are consistent with the conclusion from the SHG study.<sup>15</sup>**

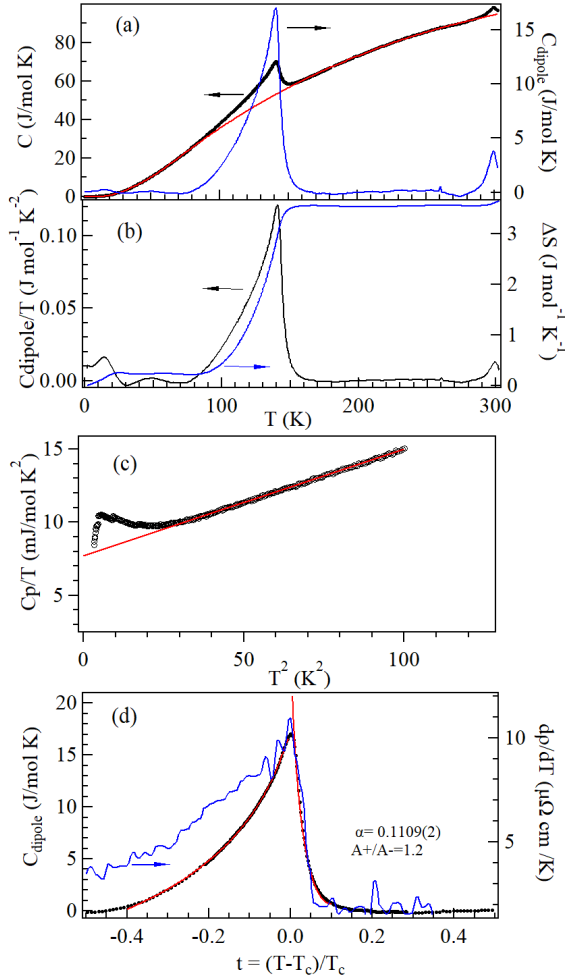


Fig.4 (a) Temperature dependence of specific heat for LiOsO<sub>3</sub>. Red line in (a) is the  $C_{\text{latt}}$  by obtained by fitting the  $C_p$  to the Debye-Einstein model. The contribution to  $C_p$  from the dipole ordering,  $C_{\text{dipole}}$ , is obtained by subtracting  $C_{\text{latt}}$  from the original  $C_p$  plotted in (a) on the left vertical axis. (b) The entropy change  $\Delta S$  associated with the transition to the polar phase is calculated by integrating  $C_{\text{dipole}}/T$  over temperature. (c) The plot of  $C_p/T$  versus  $T^2$ ; red line in (c) is the result of a linear fitting to a part of the curve of  $C_p/T$  versus  $T^2$ . (d) The plot of  $C_{\text{dipole}}$  and  $dp/dT$  versus reduced temperature. Red lines in (d) are the fitting result of  $C_{\text{dipole}}$  to the formula of the critical behavior. **The derivative  $dp/dT$  from  $p(T)$  in Fig.1 is superimposed in (d). In some ferromagnetic metals like SrRuO<sub>3</sub> and Ni, profile of the  $C_{\text{mag}}$  anomaly near ferromagnetic transition  $T_c$  matches  $dp(T)/dT$  well. See the text for the detailed discussion.**

Another important observation is that the profile of  $\Delta C_p = C_{\text{dipole}}$  in the vicinity of  $T_s$  resembles  $d\rho/dT$  in Fig.4(d). The similarity of the critical behavior between  $\Delta C_p(T)$  and  $d\rho(T)/dT$  has also been reported in the polar metal  $\text{Cd}_2\text{Re}_2\text{O}_7$ .<sup>38</sup> For conducting electrons interacting with the ion displacement in the polar semiconductor  $\text{Pb}_{1-x}\text{Ge}_x\text{Te}$ , a logarithmic increase of the resistivity has been predicted in a model that treats carriers scattering by the two-level system.<sup>17</sup> The model of Kondo-like resistivity has been applied to explain the resistivity upturn at the polar transition in  $\text{Ca}_{1-x}\text{Sr}_x\text{TiO}_3$ .<sup>20</sup> The resistivity drop on cooling through  $T_s$  in  $\text{LiOsO}_3$  resembles the resistivity drop at  $T_c$  in metallic ferromagnets such as  $\text{Ni}$ <sup>39</sup> and  $\text{SrRuO}_3$ <sup>21 40</sup> where conduction electrons interact with the array of spins. Moreover, identical critical behaviors in  $d\rho(T)/dT$  and  $C_{\text{mag}}(T)$  can also be found in these systems. Fisher and Langer<sup>41</sup> have showed that  $d\rho/dT$  is proportional to the magnetization energy  $|M_0(T)|^2$  at  $T < T_c$  and the short-range spin fluctuations at  $T > T_c$ , therefore, a  $d\rho/dT \sim C_{\text{mag}}$  is expected. A dipole analog of the Fisher-Langer theory is needed to explain the resistivity drop on cooling through the polar transition in  $\text{LiOsO}_3$ .

#### IV Magnetic property

The magnetic properties of  $\text{LiOsO}_3$  were measured with a superconducting quantum interference device (SQUID) magnetometer from Quantum Design. The contribution from the sample's holder was subtracted with the background subtraction function imbedded in the Multiview program. The paramagnetic susceptibility  $\chi(T)$  of  $\text{LiOsO}_3$  in Fig.5(a) is nearly identical to that reported in the literature.<sup>3</sup> The transition at  $T_s$  marks a transformation from a  $\chi(T)$  with a  $d\chi/dT > 0$  at  $T > T_s$  to the Curie-Weiss behavior at  $T < T_s$ ; both behaviors contradict the simple Pauli paramagnetism for free electron gas. In a solid, the band effect introduces a temperature-dependent correction to the Pauli paramagnetic susceptibility  $\chi_0$ , *i.e.*  $\chi(T) = \chi_0(1 \pm aT^2)$ ,  $a = \frac{\pi^2}{6} \left( \frac{N(\epsilon_F)''}{N(\epsilon_F)} - \left( \frac{N(\epsilon_F)'}{N(\epsilon_F)} \right)^2 \right)$ , where  $N(\epsilon_F)$  is electron DOS at the Fermi energy.<sup>42</sup> Positive sign in the formula corresponds to the case where  $\epsilon_F$  is located at a minimum of  $N(\epsilon)$ , whereas negative sign is applied to the case where  $\epsilon_F$  is located at a maximum of  $N(\epsilon)$ . A transition from a phase with  $\chi(T) = \chi_0(1 + aT^2)$  to a phase with  $\chi(T) = \chi_0(1 - aT^2)$  can create an acute minimum of  $\chi(T)$  that resembles the change of  $\chi(T)$  for  $\text{LiOsO}_3$  on crossing  $T_s$ . The behavior change of  $\chi(T)$  at  $T_s$  can indeed be justified by the change of DOS from a local maximum at  $E_F$  in the polar phase to a local minimum at  $E_F$  in the non-polar phase from a first-principles calculation for  $\text{LiOsO}_3$ .<sup>7</sup>

Whereas the  $\chi(T)$  at  $T > T_s$  cannot be fit perfectly to  $\chi(T) = \chi_0(1 + aT^2)$ , a good fit for  $\chi(T)$  at  $T < T_s$  can only be obtained to the formula  $\chi(T) = \chi_0(1 - aT^2) + C/T$  as shown in Fig.5(a). The components of band electron magnetic susceptibility and the Curie-Weiss term in fitting the  $\chi(T)$  at  $T < T_s$  are shown separately in Fig.5(b). The Curie-Weiss behavior dominates only at low temperatures. A  $\mu_{\text{eff}} = 0.12 \mu_B$  calculated from the Curie-Weiss term is far less than the spin-only value for localized electrons. In the unified theory of Curie-Weiss law for metals, Moriya has

shown that  $C$  in the new Curie-Weiss law is not related to the localized moment but the  $N(\epsilon_F)$ .<sup>43</sup> The transition to the polar phase in  $\text{LiOsO}_3$  appears to enhance electron correlations which introduce the ingredient of a Curie-Weiss behavior in the magnetic susceptibility. The effect of strong electron correlations is also reflected in  $\chi(T)$  at  $T > T_s$ . An identical temperature independent  $\chi_0 \approx 2.1 \times 10^{-4}$  emu/mol was obtained from the fittings at both  $T > T_s$  and  $T < T_s$ . With a  $\chi_{\text{Pauli}} = 6.4 \times 10^{-5}$  emu/mole calculated based on the band structure of  $\text{LiOsO}_3$ ,<sup>3</sup> a large ratio  $\chi_0/\chi_{\text{Pauli}} \approx 3.5$  is a clear indication of strongly correlated electrons in  $\text{LiOsO}_3$ . Although electron correlations result in enhancements of both  $\chi_0$  and  $\gamma_0$  relative to that based on the band structure, the enhancement of  $\chi_0$  in a ferromagnetically coupled system is much more than that in an antiferromagnetically coupled system. For example,  $\eta = (\chi_0/\chi_{\text{Pauli}})/(\gamma_{\text{exp}}/\gamma_{\text{cal}}) = 2.45$  is obtained for the Stoner enhanced,  $1/4$ -filled  $\text{LaNiO}_3$ , whereas  $\eta = 1$  is for the mass enhanced,  $1/2$  filled  $\text{LaCuO}_3$ .<sup>34</sup> An  $\eta = 1.3$  indicates that  $\text{LiOsO}_3$  is a strongly correlated system with antiferromagnetic coupling which is consistent with the  $t_2^3$  electron configuration for  $\text{Os}^{5+}$  in the oxide. Identification of strong correlations in  $\text{LiOsO}_3$  from results of specific heat and magnetization measurements is consistent with the conclusion that  $\text{LiOsO}_3$  is at crossover from itinerant to localized electronic behavior from the infrared spectroscopy study<sup>16</sup> and the first-principles calculation.<sup>10</sup>

Like Fig.5(a), the  $M(T)$  data originally reported<sup>3</sup> do not show any sign of magnetic ordering in the magnetization measurement at  $T > 2$  K. Neutron diffraction did not reveal any magnetic moment  $M \geq 0.2 \mu_B$  at  $T > 10$  K. In the  $\mu\text{SR}$  experiments on  $\text{LiOsO}_3$  with zero field and longitudinal field, the fluctuations of the moment on  $\text{Os}^{5+}$  slow down below 1.4 K, but the moments remain dynamic down to 0.08 K.<sup>44</sup> The extremely weak magnetization of  $\text{LiOsO}_3$  makes it necessary for applying a high magnetic field that may diminish any features deviating from the Curie-Weiss behavior at low temperatures. At a magnetic field below 100 Oe, the magnetic response from the  $\text{LiOsO}_3$  sample is in the same level as the contribution from the sample holder in the magnetization measurement with the MPMS. Measurements with the background subtraction function at low magnetic fields in this study reveal a well-defined dipole in a DC scan. The  $M(T)$  for  $H \leq 100$  Oe show a weak anomaly near 3 K in Fig.5(c). The cusp feature and the overlap between field cool and zero-field cool may suggest an antiferromagnetic ordering without spin canting. The magnetic ordering may also be the primary source for the hump at low temperatures in the plot of  $C_p/T$  versus  $T^2$  in Fig.4(c). Since the anomaly near 3 K only appears at low fields, we cannot rule out the possibility that it comes from a tiny amount of impurities in the sample. It is also worth noting that all possible impurity phases such as Os metal and  $\text{OsO}_2$  do not show any anomalies in their  $M(T)$  near 3 K. It is also important to note that the magnetic susceptibility of  $\text{LiOsO}_3$  is field-dependent, at least for  $H \leq 1000$  Oe in Fig.5(c). A non-linear  $M(H)$  of  $\text{LiOsO}_3$  indicates that spins undergo some kind of ordering even at  $T > 3$  K.

It remains an interesting dialog of whether  $\text{LiOsO}_3$  becomes magnetic. The enhanced  $\gamma_0$  and  $\chi_0$  and the Kadowaki-Woods ratio indicate clearly that  $\text{LiOsO}_3$  is a strongly correlated system. The

anomaly in  $M(T)$  near 3K and the broad hump at low temperatures in the plot of  $C_p/T$  versus  $T^2$  seem to support some kind of magnetic ordering. By using the LSDA+U method, He *et al.* predicted that the chemically stoichiometric  $\text{LiOsO}_3$  should be a G-AFM semiconductor. The magnetism disappears for the Li deficient  $\text{Li}_{1-x}\text{OsO}_3$  which is a metal. The lithium deficiency has been indeed verified in the  $\text{LiOsO}_3$  sample by refining neutron powder diffraction.<sup>3</sup> On the other hand, the effect of the spin-orbit coupling is generally to suppress any magnetic orderings as calculated for  $\text{LiOsO}_3$  by Zhang *et al.*<sup>45</sup>  $\text{LiOsO}_3$  should also be a Hund's metal from the  $t_{2g}^3$  configuration. The role of a Hund's coupling  $J_H$  is to make a frustrated spin or spin frozen state.<sup>24 46</sup> The weak anomaly found in  $\chi(T)$  near 3 K at a low magnetic field and a non-linear  $M(H)$  at low temperatures may result from the competition among electron-electron correlations, the spin-orbit coupling, and the Hund's coupling. It is also important to note that the chemical stoichiometry in  $\text{LiOsO}_3$  may alter the magnetic property. A further study is needed in order to have a completed understanding of magnetic state in  $\text{LiOsO}_3$  at low temperatures.

Ferroelectric  $\text{LiOsO}_3$  with strongly correlated electrons may exhibit a unique nonlinear optical property as predicted by Fu<sup>47</sup> as factors like parity breaking and strong spin-orbit coupling are taken into account. Whereas whether an antiferromagnetic order breaks the time reversal symmetry remains under debate, it would be interesting to explore the optical properties below 2.4 K in  $\text{LiOsO}_3$  where both inversion symmetry and time reversal symmetry are broken.

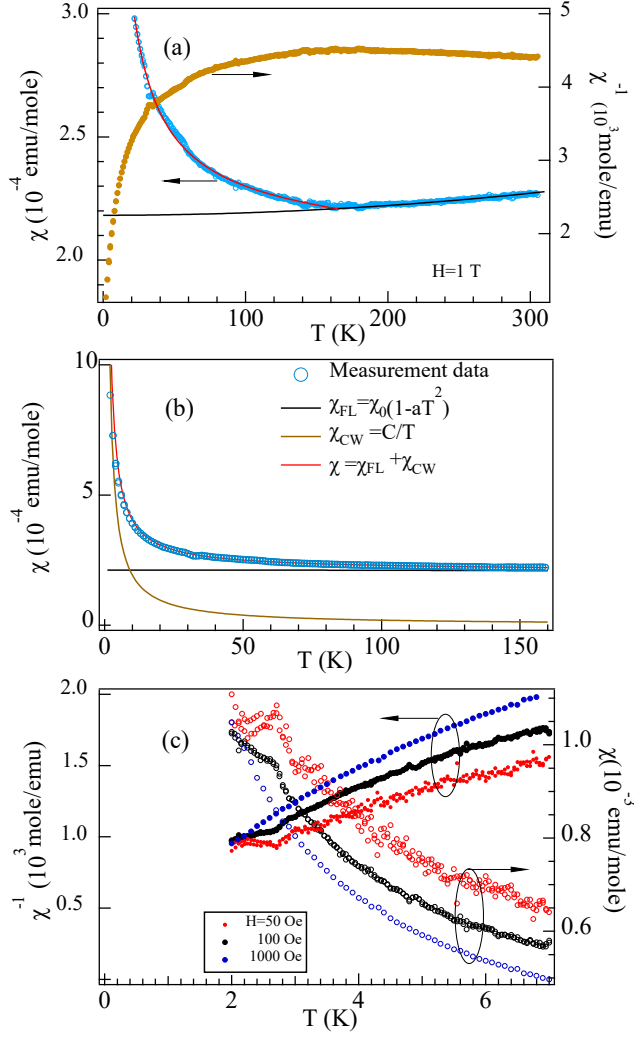


Fig.5 Temperature dependence of magnetic susceptibility  $\chi(T)$  for  $\text{LiOsO}_3$ , (a) with a high magnetic field, (b) the fitting curve and its components to the  $\chi(T)$  in (a); (c) with low magnetic fields.

## V. Thermal conductivity

The measurement of thermal conductivity  $\kappa(T)$  of  $\text{LiOsO}_3$  was made by the steady state method on small bars of polycrystalline samples. The results are highly repeatable. Since  $\text{LiOsO}_3$  is a metal, the up-bound contribution  $\kappa_e$  from electrons to the total thermal conductivity can be evaluated by the Wiedemann-Franz law based on the resistivity data in Fig.1.  $\text{LiOsO}_3$  is a bad metal, so that  $\kappa_e$  is negligibly small in comparison to the lattice contribution  $\kappa_{ph}$ . Fig.6 shows the temperature dependence of  $\kappa_{ph}$  below room temperature. A  $\kappa = 10.4 \text{ W m}^{-1}\text{K}^{-1}$  at room temperature is at the high-end value among the  $\text{ABO}_3$  oxides;<sup>48 49 50 51 52 53 54</sup> but the temperature dependence of  $\kappa$  indicates a glassy thermal conductor in the non-polar phase. A relatively sharp minimum of  $\kappa(T)$  is clearly visible in the vicinity of the critical temperature  $T_s$  followed by a



huge peak centering at 30 K. The phonon thermal conductivity of  $\kappa(T)$  in  $\text{LiOsO}_3$  below 50 K is comparable to that of a diamagnetic  $\text{LaGaO}_3$  crystal;<sup>53</sup> but the  $\kappa$  of  $\text{LiOsO}_3$  peaking at a higher temperature than that for  $\text{LaGaO}_3$  crystal means that the crystal quality of  $\text{LiOsO}_3$  is slightly low relative to that of the  $\text{LaGaO}_3$  crystal used in an early study.

The phonon thermal conductivity of  $\text{LiOsO}_3$  below  $T_s$  can be essentially described by a gas model overall. The large peak of  $\kappa_{ph}$  at low temperatures reflects the phonon-phonon, phonon-impurity, phonon-grain boundary scatterings; these scatterings are covered in the Debye formula.<sup>55</sup>

$$\kappa_{ph}(T) = \left(\frac{k_B}{2\pi^2v}\right)\left(\frac{k_B}{\hbar}\right)^3 T^3 \int_0^{\Theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} \tau(\omega, T) dx \quad (2)$$

where  $x = \hbar\omega / k_B T$ ,  $v$  is the phonon velocity, and  $\tau(\omega, T)$  is the relaxation time of a phonon, which can be expressed as

$$\tau^{-1} = \frac{v}{L} + A\omega^4 + B\omega^3 T e^{(-\Theta_D/bT)} \quad (3)$$

The first term in Eq.(3) is related to phonon scattering at the sample's boundary, the second is about scattering at defects, and the third is the phonon-phonon scattering. The phonon-phonon scattering dominates  $\kappa_{ph}$  at high temperatures whereas the effects due to scatterings at the sample's boundary or at impurities become obvious at low temperatures. The Debye temperature  $\Theta_D = 470$  K used in the fitting is from the specific heat result. As superimposed in Fig.6, the fitting curve to the Debye formula matches the essential feature of the  $\kappa_{ph}$  peak at low temperatures and the fitting parameters are given in Table 1. One of the remarkable differences of  $\kappa_{ph}$  for  $\text{LiOsO}_3$  in comparison with  $\text{LaGaO}_3$  and other crystalline oxides<sup>54</sup> is a surprisingly small  $L$  (for the boundary scattering) in the first term of Eq.3. Since the textured crystal used consists of large size ( $\sim 200$   $\mu\text{m}$ ) crystal grains, the boundary scattering in the sample should not be much different from other single crystal oxides. In a ferroelectric crystal, phonons may experience extra scatterings at the ferroelectric domain boundaries, which has been demonstrated in other ferroelectric oxides  $\text{LiTaO}_3$ <sup>54</sup> and  $\text{BiFeO}_3$ .<sup>56</sup>

The glassy  $\kappa_{ph}$  of  $\text{LiOsO}_3$  occurs at  $T > T_s$ . The phonon thermal conductivity can be generally expressed by  $\kappa_{ph} = \frac{1}{3} C_{ph} v l$ , where  $C_{ph} \sim C_p$  is the lattice heat capacity,  $v$  is the sound velocity, and  $l$  is the phonon-mean free pass. A glassy  $\kappa_{ph}$  indicates that the mean free path  $l$  is limited to the phonon-phonon scattering at the level of interatomic distance. In this case, the temperature dependence of  $\kappa_{ph}$  is basically determined by  $C_{ph}(T)$ .<sup>55</sup> A curve of  $\kappa = k C_{ph}$  is superimposed in Fig.6, which indeed matches the general trend of the glassy  $\kappa_{ph}$  at  $T > T_s$  very well. The randomness of Li ions distributed on the 12c position in the crystal structure is responsible for

the phonon scattering at the level of interatomic distance in the non-polar phase. In contrast, the phonon thermal conductivity has been found in both the paraelectric and ferroelectric phases in the displacive transition of  $\text{PbTiO}_3$ .<sup>57</sup> The remarkable transition from a glassy  $\kappa_{\text{ph}}$  to a phonon-like  $\kappa_{\text{ph}}$  at  $T_s$  is a solid proof of an order-disorder transition in  $\text{LiOsO}_3$  as a similar  $\kappa(T)$  has been found in other ferroelectrics<sup>58</sup> where an order-disorder transition occurs. It should be noticed that a glassy  $\kappa_{\text{ph}} \sim 10 \text{ Wm}^{-1}\text{K}^{-1}$  at room temperature for  $\text{LiOsO}_3$  is much higher than a typical glassy  $\kappa_{\text{ph}}$  seen in other oxides.<sup>52,53</sup> This difference could be accounted for by a relatively high sound velocity  $v$  in  $\text{LiOsO}_3$ .

The  $\kappa_{\text{ph}}$  of  $\text{LiOsO}_3$  undergoes a clear dip in the vicinity of  $T_s$ , which has not been seen in any ferroelectric insulators to our knowledge.<sup>57-59</sup> **The data will be useful to test any microscopic models to describe the influence of critical fluctuations near a ferroelectric transition on thermal conductivity, which are not available yet. It is interesting to compare the influence of dipole critical fluctuations on thermal conductivity with that by spin fluctuations.** In magnetic insulators, spin critical fluctuations near a spin ordering temperature disturb the heat transportation via phonons. Stern<sup>60</sup> has taken the Heisenberg exchange interaction which is modulated by lattice vibrations, to account for a dip of  $\kappa(T)$  commonly found in magnetic insulators. The effect of spin fluctuations on  $\kappa_{\text{ph}}$  enters the second term in Eq.3 as  $(B_1+B_2T^2C_{\text{mag}})\omega^4$ , where  $B_1$  and  $B_2$  are constants, and  $C_{\text{mag}}$  is the heat capacity for spins. For  $x < 1$  in Eq.2, a  $\kappa_{\text{ph}} \propto (B_1+B_2T^2C_{\text{mag}})^{-3/4}$  can be obtained. By taking the  $C_{\text{mag}}$  from the specific heat measurement, Stern<sup>60</sup> and later Lewis and Saunders<sup>61</sup> can account for a dip of  $\kappa_{\text{ph}}$  near  $T_N$  qualitatively. Under an assumption that dipoles act as spins in terms of the effect of critical fluctuations on the phonon transport, we can have a dipole version of the Stern's formula,  $\kappa_{\text{ph}} = (B_1+B_2T^2C_{\text{dipole}})^{-3/4}$  in the narrow temperature range around  $T_c$ . As shown in Fig.6 and more clearly in the inset, the simulated  $\kappa_{\text{ph}}$  can account stunningly well for the essential feature of the critical behavior of  $\kappa_{\text{ph}}$  near  $T_c$ .

One may be curious of why a dip of  $\kappa(T)$  at  $T_c$  has not been found in other ferroelectrics like  $\text{KH}_2\text{PO}_4$  and  $\text{KH}_2\text{AsO}_4$  which also show a glassy  $\kappa(T)$  in the non-polar phase and a phonon  $\kappa(T)$  in the polar phase.<sup>58</sup> These early-day measurements do not have a sufficiently high number of sampling points near  $T_c$ . Most importantly, these ferroelectrics are insulators. The dip of  $\kappa(T)$  found in  $\text{LiOsO}_3$  may reflect the interplay between free electrons and critical fluctuations of dipoles.

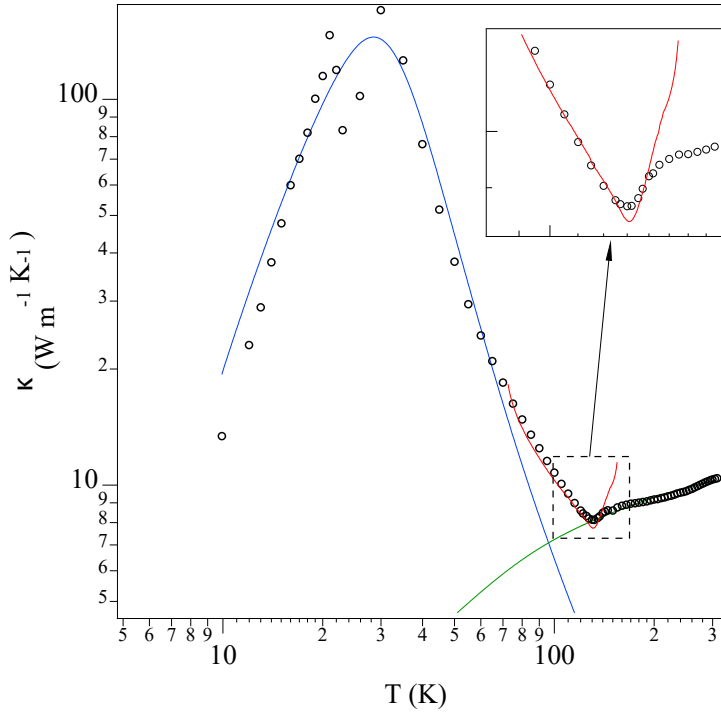


Fig.6 Temperature dependence of thermal conductivity for  $\text{LiOsO}_3$ ; the inset is a zoom-in plot showing the detail near the transition at  $T_s$ . Lines in the plot are the fitting results to the Debye formula at  $T < 50$  K and the general formula of  $\kappa$  (basically from  $C_p$ ) at  $T > 160$  K; the line in the vicinity of  $T_s$  is scaled from the Stern's formula of critical behavior for  $\kappa$ .

Table I The fitting parameters in the curve fitting of  $\kappa(T)$  in  $\text{LaGaO}_3$  and  $\text{LiOsO}_3$  to the Debye formula in Eq.2

	$\text{LaGaO}_3$	$\text{LiOsO}_3$
$v$ (m/s)	4230	4022
$\Theta_D$ (K)	554	470
$A$ ( $\text{s}^3$ )	$4.705 \times 10^{-44}$	$1.88 \times 10^{-44}$
$B$ ( $\text{K}^{-1} \text{s}^2$ )	$6.351 \times 10^{-31}$	$5.7 \times 10^{-30}$
$b$	6.031	2.36
$L$ (m)	$1.0 \times 10^{-4}$	$8.8 \times 10^{-6}$

## VI. Conclusion

$\text{LiOsO}_3$  provides an excellent example to study how itinerant electrons respond to dipole dynamics, fluctuations, and ferroelectric ordering; it is a rare ferroelectric metal with strongly correlated electrons.  $\text{LiOsO}_3$  is an n-type metal in both polar and non-polar phases. While the

monotonic temperature dependence of the thermoelectric power at  $T < T_s$  is close to the behavior of the diffusive formula, the slope is significantly enhanced relative to the prediction based on the band structure. The thermoelectric power at  $T > T_s$  cannot be accounted for by any models for metals. Strong correlations of electrons in  $\text{LiOsO}_3$  are reflected in enhancements of  $\gamma$  and  $\chi_0$  relative to the predictions from the band structure **as well as the Kadowaki-Woods ratio**. The ratio  $(\chi_0/\chi_{\text{Pauli}})/(\gamma_{\text{exp}}/\gamma_{\text{cal}}) = 1.3$  indicates an antiferromagnetic coupling in the strongly correlated  $\text{LiOsO}_3$ . As for the effect of dipole ordering to the lattice dynamics, the thermal conductivity  $\kappa$  shows a remarkable change from a glassy to a phonon-like state at the non-polar to polar transition, which indicates conclusively an order-disorder transition at  $T_s$ . The analysis of phonon thermal conductivity in the polar phase reveals that phonons are scattered at ferroelectric domain boundaries in addition to grain boundaries. Like ferromagnetic metals, the profile of  $dp/dT$  matches that of  $\Delta C = C_p - C_{\text{latt}}$  near  $T_s$  in  $\text{LiOsO}_3$ . The influence of critical fluctuations of dipoles on the thermal conductivity resembles that in antiferromagnetic insulators. These findings are useful to test theories of critical behaviors for ferroelectric metals.

## ACKNOWLEDGMENTS

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