Non-linear Temperature Dependence of Resistivity in Single Crystalline Ag₅Pb₂O₆

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We measured electrical resistivity, specific heat and magnetic susceptibility of single crystals of highly conductive oxide ${\rm Ag_5Pb_2O_6}$, which has a layered structure containing a Kagome lattice. Both the out-of-plane and in-plane resistivity show T^2 dependence in an unusually wide range of temperatures up to room temperature. This behavior cannot be accounted for either by electron correlation or by electron-phonon scattering with high frequency optic phonons. In addition, a phase transition with a large diamagnetic signal was found in the ac susceptibility, which strongly suggests the existence of a superconducting phase below 48 mK.

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I. INTRODUCTION

One of the central issues of solid state physics in recent decades has been the physics of electron-electron (e-e) correlation. As a hallmark of the Fermi liquid state formed by strong electron correlations, the resistivity exhibits T^2 dependence at low temperatures, as in many heavy-fermion systems¹. T^2 dependence of resistivity also appears in quasi-2-dimensional Fermi liquid of oxides such as Sr₂RuO₄², which is strongly suggested as a spin-triplet superconductor with $T_{\rm c}=1.5$ K. Interestingly, a layered compound MgB2, which shows superconductivity at $T_c = 39 \text{ K}^3$, also exhibits T^2 dependence in the resistivity up to 240 K^{4,5}. The $\rho \propto T^2$ law in MgB₂ is attributed not to the e-e correlation, but to the strong electron-phonon (e-ph) coupling between a quasi-2-dimensional conduction band and an optic phonon mode in the boron honeycomb layer⁶.

As another example of a layered system which exhibits T^2 resistivity, but in a much wider temperature range up to room temperature, we report here the physical properties of a layered oxide ${\rm Ag_5Pb_2O_6}$. This material was first reported by A. Byström and L. Evers in 1950^7 . As shown in Fig. 1, the crystal structure consists of an alternating stacking of Kagome layers of silver and honeycomblike networks of ${\rm PbO_6}$ octahedra, which is connected by one-dimensional chains of silver penetrating the layers. As a whole, ${\rm Ag_5Pb_2O_6}$ forms a hexagonal $P\bar{3}1m$ structure with lattice parameters $a=b=5.9324(3)\,\text{Å}$ and $c=6.4105(4)\,\text{Å}^8$.

Far before the report of the $\rho \propto T^2$ law, it was suggested by B. Dickens that $Ag_5Pb_2O_6$ shows metallic conductivity⁹, and it was confirmed by M. Jansen et al. in polycrystalline samples⁸. Band calculation by T. D. Brennan et al. revealed that its Fermi level is located near the center of the band and that its conductivity is attributed to one free electron from one formula unit, de-localized to all over the silver substructure; thus its valence formula is represented as $(Ag_5)^{4+}(Pb^{4+})_2(O^{2-})_6^{10}$. The T^2 dependence of the resistivity up to room temperature for the out-of-plane re-

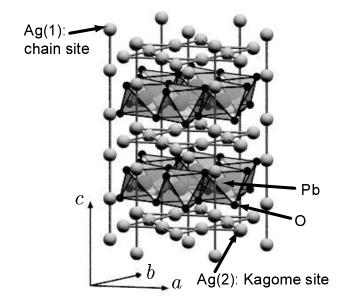


FIG. 1: Crystal structure of Ag₅Pb₂O₆.

sistivity of single crystals was recently reported by Shibata $et\ al.$ at meetings of the Physical Society of Japan 11. This dependence is rather unusual, because resistivity of almost all metals show T-linear dependence around room temperature due to the dominance of e-ph scattering.

It was Jansen et al. who first succeeded in controlled synthesis of polycrystalline $Ag_5Pb_2O_6$ by high oxygen pressure method⁸. Recent report by H. Abe et al. on a new method to obtain single crystals¹², made it possible to perform more precise experiments. Nevertheless, so far no article on experiments with single crystals has been published, although there are several articles on closely related materials, such as Bi and In substitution to the Pb site¹³, Cu substitution to the Pb site¹⁴ and $Ag_5Pb_2O_6$ with defects¹⁵. We note that there are also articles on powder samples by D. Djurek et al. reporting several strange properties^{16,17}, which have not been reproduced by other groups to the best of our knowledge.

We present here the first report on physical properties of single crystalline ${\rm Ag_5Pb_2O_6}$. We synthesized the single crystals and measured resistivity, specific heat and magnetic susceptibility. In resistivity, we succeeded not only in reproducing the T^2 dependence of the out-of-plane resistivity, but also in finding the same dependence of the in-plane resistivity for the first time. We will discuss the possible origin of the unusual T^2 resistivity. What is more, we found a large signal of diamagnetic phase transition around 48 mK, which implies that bulk superconducting phase exists in ${\rm Ag_5Pb_2O_6}$.

II. EXPERIMENTS

The single crystals of Ag₅Pb₂O₆ used in this study were grown by basically the same method as the one Shibata et al. reported¹¹. As starting materials, we used AgNO₃ (99.9999%) and Pb(NO₃)₂ (99.999%). We ground them in a mortar, and put the powder into thin Al_2O_3 crusibles with a 10-mm inner diameter. The ratio of Ag and Pb is basically stoichiometric. The crusibles were heated in air to 80°C and kept for 3 hours, then heated up to 300°C in 8 hours and up to the reaction temperature at 394°C in another 5 hours. We note here that one should cover the crusibles with larger crusibles or something in order to avoid pollution of the furnace, since melting AgNO₃ sometimes splashes out of the crusibles. The temperature was kept at this temperature for 48 hours, and the crusibles were furnace-cooled to room temperature¹¹.

However, the crystals obtained with the above parameters do not have well-defined shapes as shown in Fig. 2(a) thus they are not suitable for resistivity measurements. We found that we can grow better-shaped crystals by choosing lower reaction temperatures. Furthermore, we also discovered that adding extra AgNO₃ promotes the growth, because AgNO₃, which melts at 212°C, apparently plays a role of self-flux. Figure 2(b) shows the crystals grown with twice amount of AgNO₃ and with a reaction at 380°C. Using this process, we obtained crystals in the shape of hexagonal sticks, which are shown in Fig. 2(c)(d). The long axis of the sticks are along the c axis. The largest size of crystals was approximately 1 mm in length and 0.5 mm in thickness.

For characterization of the obtained crystals, we used powder X-ray diffractmetry with $\text{CuK}\alpha_1$ radiation, which confirmed that these crystals were single-phased $\text{Ag}_5\text{Pb}_2\text{O}_6$. Resistivity was measured using a standard four-probe method with dc or ac current. Specific heat was measured with a commercial calorimeter (Quantum Design, model PPMS), and dc susceptibility by a SQUID magnetometer (Quantum Design, model MPMS). AC susceptibility was measured by a mutual inductance method down to 38 mK using a $^4\text{He-}^3\text{He}$ dilution refrigerator.

We note here about the lowest temperature of the resistivity measurement. We used an ultrasonic soldering

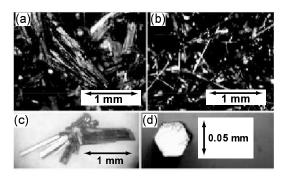


FIG. 2: Photos of single crystals of Ag₅Pb₂O₆ taken with optical microscopes. The long axis of these crystals are along the c axis. (a) Single crystals in a crusible which are obtained with basic reaction parameters described in the text. (b) Single crystals at the bottom of a crusible when we mixed AgNO₃ and Pb(NO₃)₂ with a ratio of Ag:Pb=5:1 and also chose a lower reaction temperature (380°C). The crystals grew dispersed from each other and the shapes became better with the aid of self-flux AgNO₃. In this case AgNO₃ little remained since most of unreacted AgNO₃ had been evaporated or resolved into Ag metal. (c) A group of single crystals removed from the crusible in photo (b). We obtained a lot of crystals with a perfectly hexagonal-stick shape by adding self-flux AgNO₃. (d) A cross section of a typical single crystal (not the largest). This hexagonal plane is in the ab plane of $Ag_5Pb_2O_6$.

method to attach the leads to the crystals, because several conductive pastes (e.g. silver paste) we used all damaged the sample seriously. On the other hand, the solder we used (Cerasolzer #123, Senju Metal Industry) becomes superconducting below 3 K, which makes it impossible for us to measure the sample resistivity accurately below 3 K. We should also note that the accuracy of in-plane resistivity is less reliable than that of the out-ofplane resistivity. This is because we could not shape up the samples before attaching leads to the crystal. Thus the electric current did not flow uniformly and we could not determine ρ by the simple relation as $\rho = R(S/l)$, where S is the cross section and l is the lead spacing. The results of ρ_{ab} shown in Fig. 3 is an estimation assuming uniform current flow. Nevertheless, the relative variation of ρ in temperature should be reliable.

III. RESULTS

Figure 3 shows the resistivity along the c axis (ρ_c) and in the ab plane (ρ_{ab}) . Anisotropy of resistivity at 280 K is rather small and approximately 2, which is consistent with the results of the band calculation by Brennan et $al.^{10}$ The residual resistivity for ρ_c and ρ_{ab} are 9.7 $\mu\Omega$ cm and 1.5 $\mu\Omega$ cm, respectively; this means residual resistivity ratio (RRR) are 35 for ρ_c and 93 for ρ_{ab} , which show that the quality of the samples was quite good. If we assume its temperature dependence as

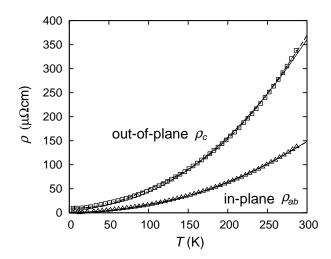


FIG. 3: Temperature dependence of the out-of-plane (open squares) and the in-plane resistivity (open triangles) down to 3 K. Solid lines are the fitting with $\rho(T) = \rho_0 + A'T^p$ with p = 2.13 for ρ_c and p = 2.11 for ρ_{ab} . Dashed lines are the fitting assuming the existence of a Einstein-like optic phonon mode.

 $ho(T)=
ho_0+A'T^p$, we obtained the exponent as p=2.13 for ho_c and p=2.11 for ho_{ab} from the fitting in all temperature range¹⁸. For both direction, p is close to 2; thus if we approximate as $ho(T)=
ho_0+AT^2$, we obtained the coefficient of T^2 term $A_c=3.78\times 10^{-3}~\mu\Omega {\rm cm/K}^2$ for $ho_c(T)$ and $A_{ab}=1.6\times 10^{-3}~\mu\Omega {\rm cm/K}^2$ for $ho_{ab}(T)$.

The measured specific heat is shown in Fig. 4. Since ${\rm Ag_5Pb_2O_6}$ does not contain any magnetic ions, we express C_P in 1-mol formula unit, in other words, of 1-mol conduction electrons. In high temperature region, C_P converges to a constant value, which agrees with Dulong-Petit's classical phonon specific heat, $C_{\rm cl}=3k_{\rm B}rN_{\rm A}=324~{\rm J/K~mol^{19}},$ where r=13 is the number of atoms in one formula unit. We also measured the specific heat in magnetic fields, but there was no difference between the data in 0 T and in 7 T. The inset is the C_P/T -vs.- T^2 plot below 3.3 K. We obtained the electronic specific heat coefficient $\gamma_{\rm e}=3.42~{\rm mJ/K^2mol}$ and the Debye temperature $\Theta_{\rm D}=186~{\rm K}$ from this plot.

 $Ag_5Pb_2O_6$ displays weak constant diamagnetism in $10~{\rm K} < T < 350~{\rm K},~ (-2.07 \pm 0.02) \times 10^{-4}~{\rm emu/mol},$ from dc susceptibility measurement. Below $10~{\rm K},~\chi_{\rm dc}$ increases probably owing to paramagnetic impurities. To subtract the diamagnetic contribution from the ion cores, we used the values of the susceptibility of cores in the literature²⁰; we estimated the total contribution from the cores as $-2.44 \times 10^{-4}~{\rm emu/mol}$. When we subtracted this value from the experimental value, we obtained $(+3.7 \pm 0.2) \times 10^{-5}~{\rm emu/mol}$. This is the Pauli susceptibility of conduction electrons because there are no magnetic ions in $Ag_5Pb_2O_6$.

In the ac susceptibility measurement, we found a very large signal around 45 mK as shown in Fig. 5. The signal was reproducible in different samples, in different susceptions are succeptible in the susceptibility of the

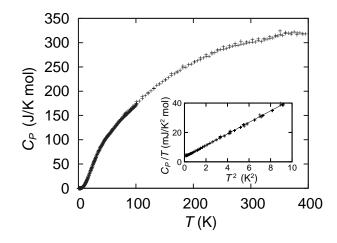


FIG. 4: Specific heat of Ag₅Pb₂O₆ down to 0.35 K. These figures contain the results of several different samples. Inset: C_P/T plotted against T^2 below 3.3 K. Solid line is the fitting $C_P(T)/T = \gamma_{\rm e} + \beta_{\rm p} T^2$ with $\gamma_{\rm e} = 3.42$ mJ/K² mol and $\beta_{\rm p} = 3.91$ mJ/K⁴ mol.

tibility cells and in different ac magnetic field amplitudes and frequencies. We also measured ac susceptibility of a bulk pure Al with approximately the same volume as the measured Ag₅Pb₂O₆ using the same cell, and found that Ag₅Pb₂O₆ yields as large a diamagnetic signal as that of the superconducting transition of Al. Moreover, this transition disappears under a few Oe magnetic field, and Ag₅Pb₂O₆ does not contain any magnetic ions which may cause a diamagnetic transition. Thus this signal strongly implies the existence of a bulk superconducting phase of Ag₅Pb₂O₆. The inset of Fig. 5 is the phase diagram of this new phase. " $H_c(T)$ " was determined from the peaks of imaginary part χ''_{ac} by sweeping magnetic field at each fixed temperature. We note that values of H in the inset of Fig. 5 is shifted because exact zero point of our magnet changed by a few Oe due to the residual magnetic field. Thus we swept magnetic field from +10 Oe to -10 Oe and determined exact zero point from the symmetry of the χ_{ac} data. " H_c " is well fitted by a parabolic law for superconductor: $H_c(T) = H_{c0}[1 - (T/T_{c0})^2]$ where $H_{\rm c0}=3.0$ Oe and $T_{\rm c0}=48$ mK obtained by fitting. This variation also supports the evidence of superconductivity.

IV. DISCUSSION

Now we discuss the origin of the T^2 dependence of resistivity. One possibility is e-e interaction. Resistivity of materials in which strong e-e correlation exists shows T^2 dependence only at temperature much lower than room temperature, because the characteristic temperature of many-body Fermi liquid formation is low and also the T^2 -behavior requires the dominance of the e-e scattering over the e-ph scattering. If the $\rho \propto T^2$ law up to room temperature of $Ag_5Pb_2O_6$ comes from the e-e correlation, the e-e correlation must be so large as to dominate over

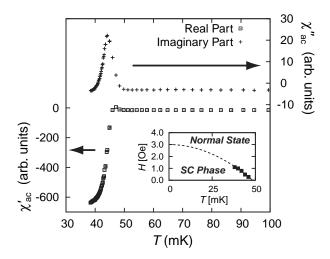


FIG. 5: AC magnetic susceptibility below 0.1 K, measured with an ac magnetic field of amplitude 2.3×10^{-2} Oe and frequency 887 Hz. A very large diamagnetic phase transition signal was found below 45 mK, which suggests the existence of a superconducting (SC) phase. Inset: Phase diagram of ${\rm Ag_5Pb_2O_6}$ below 50 mK. Closed squares are " H_c " determined from the peaks of imaginary part $\chi''_{\rm ac}$. Dashed line shows the classical parabolic law of superconductivity: $H_c(T) = H_{c0}[1 - (T/T_{c0})^2]$.

the e-ph scattering even at room temperature. But it seems impossible to expect strong e-e interaction from the discussions below. First, the electronic specific heat coefficient of Ag₅Pb₂O₆ is comparable to those of normal metals and $1 \sim 3$ orders of magnitude smaller than those of strongly-correlated electron systems. Moreover, neither the Wilson ratio nor the Kadowaki-Woods (K-W) ratio shows evidence of strong e-e correlations. The Wilson ratio, which is given by $(\pi^2 k_{\rm B}^2/3\mu_{\rm B}^2)(\chi_{\rm Pauli}/\gamma_{\rm e})$, is expected to increase from unity to 2 as e-e interaction increases from 0 to ∞^{21} . In Ag₅Pb₂O₆, the Wilson ratio is 0.79, close to unity, implying that the e-e interaction is weak. Of course we should note that the value of χ_{Pauli} may not be very accurate because the subtracted core contribution is much larger than χ_{Pauli} . The K-W ratio is defined as $A/\gamma_{\rm e}^2$ and becomes a universal value $a_0=1.0\times 10^{-5}~\mu\Omega{\rm cm}({\rm K~mol/mJ})^2$ in most strongly-correlated systems^{1,22}. The K-W ratio of Ag₅Pb₂O₆ is $32.3a_0$ for ρ_c and approximately $14a_0$ for ρ_{ab} ; both are much larger than a_0 . These deviation imply that Ag₅Pb₂O₆ cannot be classified into strongly-correlated electron systems and that the T^2 dependence of ρ is not due to e-e interaction.

Another possible origin is the e-ph scattering. Basically, resistivity governed by the e-ph interaction is T-linear above $\Theta_{\rm D}/5$ ($\approx 20 \sim 100$ K, in most metals). But there are some materials of which resistivity shows non-linear T dependence at relatively high temperature because of the e-ph scattering by high energy optic phonons. For example, MgB₂ shows $\rho \propto T^2$ behavior in $T_{\rm c} < T \lesssim 240$ K^{4,5}, and ReO₃ exhibits an unusual

curvature in the resistivity in 120 K $\lesssim T \lesssim 220 \text{ K}^{23}$. When analyzing non-linear T dependence of resistivity in these materials, it is a common approach to assume the optic phonons as Einstein-like^{6,23,24}. In this method, the Boltzmann equation is a starting point:

$$\rho(T) = \rho_0 + \frac{(4\pi)^2 k_{\rm B} T}{\hbar \omega_{\rm p}^2} \int_0^{\omega_{\rm max}} \frac{d\omega}{\omega} \alpha^2 F(\omega) \left(\frac{x}{\sinh x}\right)^2, (1)$$

where $x = \hbar \omega/2k_{\rm B}T$, $\alpha^2 F(\omega)$ is the Eliashberg function, $\omega_{\rm p}$ is the plasma frequency of conduction electrons. We assume that we can separate the Eliashberg function into the Debye term and the Einstein term:

$$\alpha^{2} F(\omega) = 2\lambda_{\rm D} \left(\frac{\omega}{\Omega_{\rm D}}\right)^{4} \theta(\Omega_{\rm D} - \omega) + \frac{\lambda_{\rm E} \Omega_{\rm E}}{2} \delta(\omega - \Omega_{\rm E}), \quad (2)$$

where $\Omega_{\rm D}$ and $\Omega_{\rm E}$ are the Debye frequency and the frequency of Einstein phonons, respectively, and λ_D and $\lambda_{\rm E}$ are the e-ph coupling constant of Debye phonons and of Einstein phonons, respectively. Now we can substitute this Eliashberg function into Eq. 1, and fit it with the experimental data. When we used $k_{\rm B}\Omega_{\rm D}/\hbar$, $k_{\rm B}\Omega_{\rm E}/\hbar$, $\lambda_{\rm D}/\omega_{\rm p}^2$ and $\lambda_{\rm E}/\omega_{\rm p}^2$ as fitting parameters, we obtained $k_{\rm B}\Omega_{\rm D}/\hbar=290$ K and $k_{\rm B}\Omega_{\rm E}/\hbar=1200$ K from the fitting with ρ_c data, and $k_{\rm B}\Omega_{\rm D}/\hbar = 280$ K and $k_{\rm B}\Omega_{\rm E}/\hbar = 1100~{\rm K}$ from ρ_{ab} . The results of the fittings are shown in Fig. 3 with dashed lines. But the existence of such a high frequency Einstein-like phonon is doubtful. This is because specific heat shown in Fig. 4 converges to Dulong-Petit's value around 350 K, implying that all phonon modes are "freely" excited at this temperature and thus there seems to be no more phonon mode with energy much larger than 350 K²⁵. For comparison, the specific heat of MgB₂, in which the optic phonon mode with a wavenumber of 620 cm^{-1} (890 K in energy) plays important roles, is indeed not at all saturated even at $300 \ {
m K}^{26}.$

If we assume that the novel phase below 48 mK is a phonon-mediated superconducting phase, we can estimate the e-ph coupling constant λ from McMillan's relation²⁷:

$$T_{\rm c} = \frac{\Theta_{\rm D}}{1.45} \exp\left[-\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)}\right].$$
 (3)

When we assumed the psudopotential as $\mu^* = 0.1$ and used $\Theta_{\rm D} = 186$ K, we obtained $\lambda = 0.288$, which is comparable to those of W ($\lambda = 0.28$, $T_{\rm c} = 12$ mK) or Be ($\lambda = 0.23$, $T_{\rm c} = 26$ mK)²⁷. Such a small λ may be another evidence that strong e-ph interaction does not exist in ${\rm Ag}_5{\rm Pb}_2{\rm O}_6$.

The unusual $\rho \propto T^2$ behavior up to room temperature thus can be attributed to neither e-e interaction nor e-ph interaction including the optic phonons. We note here that a one-dimensional chain organic compound TTF-TCNQ exhibits $T^{2.33}$ dependence of resistivity in $60 \text{ K} < T < 300 \text{ K}^{28}$, attributable to the librational phonon mode in the chain²⁹. This scenario is not applicable to $Ag_5Pb_2O_6$ because of the rigidness of the lattice

against twisting motion of the silver chain. Nevertheless, a unique phonon mode may exist also in ${\rm Ag_5Pb_2O_6}$ which gives rise to the T^2 dependence. Thus a detailed investigation into the phonon modes in ${\rm Ag_5Pb_2O_6}$ and into their strength of coupling with conduction electrons may elucidate the T^2 dependence.

V. CONCLUSION

In conclusion, we synthesized single crystals of $Ag_5Pb_2O_6$ and measured their resistivity, specific heat and magnetic susceptibility. The resistivity exhibits unusual T^2 dependence up to room temperature both along the c axis and in the ab plane. This behavior cannot be explained by e-e interaction. It seems also impossible to explain the T^2 dependence from the e-ph scattering by optic phonons. Thus there should be other scattering mechanisms in $Ag_5Pb_2O_6$. Moreover, a phase transition

with a large diamagnetic signal was found below 48 mK and below 3 Oe. This new phase seems to be a bulk superconducting phase in $Ag_5Pb_2O_6$.

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