Exceptional type-I superconductivity of the layered silver oxide \( \text{Ag}_5\text{Pb}_2\text{O}_6 \)

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We report zero-resistivity transition and the details of magnetic transition of a layered silver oxide \( \text{Ag}_5\text{Pb}_2\text{O}_6 \) single crystal, which make definitive evidence of superconductivity in this compound. In the AC susceptibility of a mono-crystal, we observed large supercooling, as well as positive peaks in the real part of the susceptibility indicating the reversibility of magnetic process. These observations reveal that \( \text{Ag}_5\text{Pb}_2\text{O}_6 \) is probably the first oxide that shows type-I superconductivity. Evaluation of the superconducting parameters not only gives confirming evidence of type-I superconductivity, but also indicates that it is a dirty-limit superconductor. We also analyze supercooling to determine the upper limit of the Ginzburg-Landau parameter.

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In the last two decades, research of oxide superconductors is one of the most actively-studied fields in solid state physics\(^{13,14} \). Copper oxide high-\( T_c \) superconductors\(^{15,16} \) discovered in 1987 made the greatest impact to the field. \( \text{Sr}_2\text{RuO}_4 \), with accumulating evidence for a spin-triplet superconductor\(^{17} \), has attracted much attention. More recently, \( \text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O} \) with a triangular lattice\(^{18} \) is widely studied because of the coexistence of superconductivity and geometrical frustration and of possible novel superconducting phenomena. We note here that the unconventional superconductors of oxides listed above have layered structures, and that it is believed a quasi-two-dimensional crystal structure is favorable for unconventional superconductivity. As possible candidates for novel unconventional superconductivity, silver oxides are particularly worth investigation, since they might have electronic structures analogous to the high-\( T_c \) cuprates. However, the only silver oxide superconductors reported so far were cubic clathrate salts \( \text{Ag}_7\text{O}_4X \quad (X=\text{NO}_3, \text{HF}_2, \text{etc.}) \), found in 1966. Curiously, no other silver oxide superconductors have been reported for nearly 40 years, let alone those with layered structures.

Here we report the discovery of superconductivity in \( \text{Ag}_5\text{Pb}_2\text{O}_6 \), with \( T_c \) of 52.4 mK, an eagerly-awaited and the very first layered silver oxide superconductor. What is more, we clarified that \( \text{Ag}_5\text{Pb}_2\text{O}_6 \) is a type-I superconductor. This fact is rather surprising, since most type-I superconductors are pure metals and only a handful are known among compounds and alloys. To the best of our knowledge, reported compound type-I superconductors are only \( \text{ZrB}_2 \), \( \text{YbSb} \), \( \text{LaPd}_2\text{Ge}_3 \), \( \text{MPd}_2\text{Si}_2 \) \((M=\text{Lu}, \text{Y}, \text{La}, \text{Li}, \text{TaSi}_2, \text{AuIn}_2, \text{C}_4\text{K}_6)\) (intercalation), \( \text{LaRh}_2\text{Si}_2 \); thus \( \text{Ag}_5\text{Pb}_2\text{O}_6 \) is the first oxide type-I superconductor.

\( \text{Ag}_5\text{Pb}_2\text{O}_6 \), which was first reported by Bystrom and Evers in 1955\(^{19} \), has a rather interesting crystal structure (see the inset of Fig.\(^1\)) consisting of a silver Kagome lattice parallel to its \( ab \) plane and silver chains along the \( c \) axis\(^{19} \). This silver oxide exhibits metallic conductivity. Band calculation by Brennan and Burdett\(^{20} \) shows that its conductivity mainly comes from \( \text{Ag}_5\text{S} \) orbital, and that its Fermi surface has a quasi-three-dimensional character because both the silver chain and Kagome lattice contribute to the density of states at the Fermi level. Interestingly, the resistivity behaves as \( \rho = AT^2 + \rho_0 \) in an unusually wide range of temperature, down to below 4 K and up to room temperature\(^{20} \). This means that unknown strong scattering mechanism dominates over the usual electron-phonon scattering. Superconductivity of \( \text{Ag}_5\text{Pb}_2\text{O}_6 \) was recently suggested by the present authors\(^{20} \). We reported quite a large diamagnetic signal in the AC susceptibility measured using a cluster of single crystals below 48 mK but could not obtain zero resistivity at that time. We finally observed zero resistivity by improving experimental techniques, and present in this paper not only the observation but also the details of superconducting properties of \( \text{Ag}_5\text{Pb}_2\text{O}_6 \) for the first time.

In the experiments, we used single crystals of \( \text{Ag}_5\text{Pb}_2\text{O}_6 \) grown by the self-flux method, from mixture...
of 5-mmol AgNO₃ and 1-mmol Pb(NO₃)₂. All the measurements reported here were performed with a ⁴He-³He dilution refrigerator (Cryoconcept, Model DR-JT-S-100-10), covering the measurement temperatures as low as 16 mK. The resistivity was measured using a conventional four-probe method with an AC current of 10.4 μA rms at 163 Hz with a hexagonal-stick single crystal which fits in 0.14 × 0.21 × 1.15 mm³. We used pure gallium to attach electrical wires of copper to the sample crystals. We note here that one must keep the temperature of the electrodes well below the melting point of gallium (29°C) all the time after soldering in order to avoid the electrical contacts getting worse. We avoided using gold wires because gallium easily dissolves gold. The AC susceptibility was measured by a mutual inductance method. We fabricated a very small and highly-sensitive cell by winding a 50-µm-diameter copper wire on a 0.5-mm-diameter polyimide tube (The Furukawa Electric Co., Ltd., PIT-S). The excitation field \( H_{\text{AC}} \) was 8.7 mOe rms at 887 Hz, which is much lower than the \( H_c \) of Ag₅Pb₂O₆. To reduce the influences of remnant magnetic fields such as the earth’s field and the residual field in the equipment, these measurements were performed in a magnetic shield. We used a cylinder of permalloy (Hamamatsu Photonics K.K., E989-28), which has an extremely high permeability. Inside the permalloy tube, we also placed a lead tube, taking into account the shielding current on lead shield’s surface.

The observed zero-resistivity transition is shown in Fig. 1. A clear zero resistivity is seen, which marks definitive evidence of superconductivity of Ag₅Pb₂O₆. We note here that the result in Fig. 1 was obtained without the magnetic shield. A hysteresis at the superconducting transition and a lower \( T_c \) than that in the AC susceptibility measurement are attributable to the influence of the uncanceled residual field. We confirmed that the hysteresis indeed disappears in the measurement with the magnetic shield. We next show in Fig. 2 the real part of the AC susceptibility \( \chi_{\text{AC}} \) of a mono-crystal with the magnetic shield described below. It is worth noting that we used the identical crystal for the measurements for Figs. 1 and 2 (see the left inset of Fig. 1). We also note here that the diamagnetic signal shown in Fig. 2 is as large as that of pure Al with a similar size and shape. Such results of the low-frequency susceptibility add a strong support for the bulk nature of the superconductivity in Ag₅Pb₂O₆. The measurements were performed under the condition \( H_{\text{DC}} \parallel H_{\text{AC}} \parallel c \). The critical temperature \( T_c \) to some extent depends on samples; the highest \( T_c \) obtained is 52.4 mK, as shown in Fig. 2.

In Fig. 2 there are two strong pieces of evidence that Ag₅Pb₂O₆ is a type-I superconductor. One is the fact that a large supercooling is observed at the superconducting transition under magnetic fields while no supercooling is seen in zero field. This means that the superconducting transition becomes first order only when an external field is applied. Such behavior is only seen in type-I superconductors. The other is the very large positive peaks of \( \chi'_{\text{AC}} \) just before the superconducting to normal transitions. These peaks are ascribable to the “differential paramagnetic effect” (DPE), which represents that the field derivative of the magnetization \( \partial M/\partial H \) is positive near the transition and also the magnetic process in this region is reversible. In a type-I superconductor with a finite size, the intermediate state takes place and the DPE should be observed. On the other hand, type-II superconductors should show no or rather small DPE because of the irreversibility of magnetic process due to flux pinning. Thus the large DPE is a hallmark of type-I superconductivity.

![Fig. 2: (color online) AC susceptibility of Ag₅Pb₂O₆. (a) Result of a temperature sweep with a sweep rate of 0.2 mK/min. The residual field \( H_{\text{res}} \) has been compensated in this sweep, yielding \( T_{\text{co}} = 52.4 \) mK. (b) Results of field sweeps at several temperatures with a sweep rate of 24-47 mOe/min. From the slight asymmetry of the data, the residual field is estimated as \( H_{\text{res}} = 0.40 \) Oe.](image-url)
The Ginzburg-Landau (GL) coherence length, $\xi_0 = (0.18 \hbar v_F)/(k_B T_c)$, is 11 µm, where $v_F = h k_F/m^*$ is the Fermi velocity, is comparable to that of tungsten\(^{24}\) ($\xi_0 = 32 \mu$m, $T_c = 15.4$ mK). The mean free path $l$ is given by $l = v_F \tau$, where $\tau$ is the scattering time of electrons and has a relation $\tau^{-1} = n e^2 \rho/m^*$ for the Drude model. If we use $\rho = 1.5 \mu$Ω cm, the residual resistivity in the $ab$ plane\(^{25}\), we obtain $l = 240$ nm.

One of the important consequences of the above evaluation is that Ag\(_5\)Pb\(_2\)O\(_6\) is a dirty-limit ($\xi_0 \gg l$) superconductor. This is rather inevitable, since it seems practically impossible to make $l$ longer than $\xi_0$. In a dirty-limit superconductor, the GL parameter $\kappa$ is given by $\kappa = 0.75 \lambda_0(0)/l$ (Ref. 27), and is 0.26 in our case. This is indeed smaller than $1/\sqrt{2}$, the border between type-I and -II superconductors, and is consistent with the type-I behavior of Ag\(_5\)Pb\(_2\)O\(_6\). The dirty-limit conclusion also implies that the pairing symmetry of the superconductivity is not anisotropic, because anisotropic superconductivity should be easily suppressed even by non-magnetic impurities.

According to the GL theory, analysis of supercooling gives the upper limit of $\kappa$. When one decreases the external field of a supercooled superconductor at constant temperature, the sample turns into the superconducting state before the field reaches the ideal supercooling field $H_{sc,ideal}$. If the sample is in vacuum, $H_{sc,ideal}$ is equal to the surface nucleation field $H_{sc}^{\text{surf}}$, which has a relation $H_{sc} = 1.695 H_{sc}^{\text{ideal}} = 1.695 \sqrt{2k_B T_c}$. The observed supercooling field $H_{sc}$ satisfies an inequality:

$$H_{sc} \geq H_{sc,ideal} = 1.695 \sqrt{2k_B T_c}. \quad (1)$$

Thus $\kappa$ must be smaller than $\kappa_{sc} \equiv H_{sc}/(1.695 \sqrt{2k_B T_c})$.

An approach based on this has been used to determine $\kappa$ of several pure metals and alloys by observing ideal supercooling. For example, Feder and McLachlan\(^{26}\) realized ideal supercooling of indium and tin with precise experiments and obtained $\kappa_{in} = 0.0620$ and $\kappa_{Sn} = 0.0926$.

We calculated $\kappa_{sc}$ of Ag\(_5\)Pb\(_2\)O\(_6\) at each temperature as shown in Fig. 4. The steep increase of $\kappa_{sc}$ close to $T_c$ is attributed to the size effect, which occurs when the temperature-dependent coherence length $\xi(T) \propto [T_c/(T_c - T)]^{1/2} \xi$ becomes comparable to the size of a sample. In fact, the coherence length, being $\xi \sim \xi_0 (0.1)^{1/2}$ in a dirty-limit superconductor\(^{27}\), becomes 1.4 µm. This is large enough to cause the size effect near $T_c$ in a sample of 100-200 µm (~100 $\xi$). Indeed, in the experiments of Feder and McLachlan\(^{28}\) a sphere of clean indium ($\xi \sim \xi_0 = 0.20$ µm) with a radius 16 µm (~80 $\xi$) showed the size effect near $T_c$.

Feder and McLachlan determined $\kappa$ by extrapolating $\kappa(T)$ to $T = T_c$, because the influence of nucleation centers becomes negligible near $T_c$ due to divergence of $\xi(T)$. Following their procedure we extrapolated $\kappa_{sc}(T)$ in 35 mK < $T$ < 47 mK to $T_c$ as the broken line in Fig. 4. The extrapolation gives $\kappa_{sc}(T = T_c) = 0.085$, which should be the upper limit of $\kappa$ of Ag\(_5\)Pb\(_2\)O\(_6\). This estimated

Figure 3 is the phase diagram based on the AC susceptibility of the crystal with the highest $T_c$. Here we identify the transition fields of the superconducting to normal transition as critical fields $H_c$. This should be valid despite the possibility of superheating, because the observed DPE shows that Ag\(_5\)Pb\(_2\)O\(_6\) is in the intermediate state, in which superconducting and normal states coexist, and there should be no superheating at the “transition” from the intermediate state to the normal state. We also define the normal to superconducting transition fields as supercooling fields $H_{sc}$. This transition should be from the normal to the full Meissner states since we observed no DPE. We can fit a relation $H_c(T) = H_{co}[1 - (T/T_{co})^\alpha]$ to all the $H_c$ data down to 16 mK using $H_{co}$ and $\alpha$ as fitting parameters, while $T_{co} = 52.4$ mK is determined from the temperature sweep data in zero field. As a result, we obtained $H_{co} = 2.19$ Oe and $\alpha = 1.56$. The data can also be fit by a conventional relation with $\alpha = 2$: $H_c(T) = H_{co}[1 - (T/T_{co})^2]$. However, the fitting is successful only down to $T/T_{co} = 0.7$ and the resulting parameter is $H_{co}^* = 1.80$ Oe.

Now we can evaluate some of the superconducting parameters from these results. First, the London penetration depth is obtained as $\lambda_L(0) = (m^* e^2/4\pi\hbar c)^{1/2} = 83$ nm. Here $n = 1.0/V_M = 0.51 \times 10^{22}$ electrons/cm$^3$ is the electron carrier density, where $V_M = 0.195$ nm$^3$ is the volume of a unit cell, and $m^* = (3\hbar^2 \gamma_e)/(k_B^2 k_F)$ is 1.2$m_e$, the effective mass. We used here the measured electronic specific heat coefficient\(^{26}\) $\gamma_e = 3.42$ mJ/mol K$^2 = 291$ erg/cm$^3$K$^2$, and the Fermi wavenumber $k_F = 4.5$ nm$^{-1}$ (in the $ab$ plane).
upper limit is smaller than the calculated value but the difference should be within a consistency. In the case of indium or tin, there are also differences of a few factors among values of \( \kappa \) obtained by different procedures.

In conclusion, we succeeded in observing zero resistivity transition of a silver oxide \( \text{Ag}_5\text{Pb}_2\text{O}_6 \), giving definitive evidence of the long-awaited layered silver oxide superconductor since the discovery of high-\( T_c \) cuprates. The AC susceptibility reveals that \( \text{Ag}_5\text{Pb}_2\text{O}_6 \) is an oxide type-I superconductor. It is widely considered that type-I superconductivity is rare in compounds, although there is no fundamental reason to prohibit it. The present discovery indeed demonstrates that even an oxide can be an extreme type-I superconductor. Superconducting parameters indicate that \( \text{Ag}_5\text{Pb}_2\text{O}_6 \) is a dirty-limit type-I superconductor and thus the pairing symmetry of \( \text{Ag}_5\text{Pb}_2\text{O}_6 \) should be isotropic. The discovery of this novel class of superconductor, silver oxide superconductor with a layered structure, should motivate searches for more superconductors among similar silver oxides. A salient next target is to adjust the doping to realize the electronic states with strong electron correlations, closely analogous to that of the high-\( T_c \) cuprates, in order to seek for unconventional superconductivity.

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FIG. 4: The ratio \( \kappa_{sc} \equiv H_{sc}/(1.695\sqrt{2}H_c) \) of \( \text{Ag}_5\text{Pb}_2\text{O}_6 \), which gives the upper limit of the GL parameter. The upper limit is smaller than the calculated value but the difference should be within a consistency. In the case of indium or tin, there are also differences of a few factors among values of \( \kappa \) obtained by different procedures.
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