Type-I superconductivity of the layered silver oxide $\text{Ag}_5\text{Pb}_2\text{O}_6$

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(Received 16 August 2005; published 28 November 2005)

We report the zero-resistivity transition and the details of the magnetic transition of a layered silver oxide $\text{Ag}_5\text{Pb}_2\text{O}_6$ single crystal, which provide definitive evidence of superconductivity in this compound. In the ac susceptibility of a monocrystal, we observed large supercooling, as well as positive peaks in the real part of the susceptibility indicating the reversibility of the magnetic process. These observations reveal that $\text{Ag}_5\text{Pb}_2\text{O}_6$ is an 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.

DOI: 10.1103/PhysRevB.72.180504 PACS number(s): 74.10.+v, 74.25.Dw, 74.70.Dd

In the last two decades, research of oxide superconductors has become one of the most actively studied fields in solid state physics.$^{1,2}$ Copper oxide high-$T_c$ superconductors$^8$ discovered in 1987 made the greatest impact to the field. $\text{Sr}_2\text{RuO}_4$, with accumulating evidence for a spin-triplet covered in 1987 made the greatest impact to the field.

Tungus to the high-temperature superconductors. As possible candidates for unconventional superconductivity than three-dimensional structures, and that it is believed a quasi-two-dimensional character because both the silver plane and silver chains along the $c$ axis. This silver oxide exhibits metallic conductivity. Band calculation by Brennan and Burdett$^{16}$ shows that its conductivity mainly comes from the $\text{Ag}_5\text{S}_5$ 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.$^{17}$ This means that an 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.$^{17}$

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 the superconducting properties of $\text{Ag}_5\text{Pb}_2\text{O}_6$.

In the experiments, we used single crystals of $\text{Ag}_5\text{Pb}_2\text{O}_6$ grown by the self-flux method, from a mixture of 5-mmol $\text{AgNO}_3$ and 1-mmol $\text{Pb(NO}_3)_2$. All the measurements reported here were performed with a $^3\text{He}-^4\text{He}$ 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 $\mu\text{A}$ rms at 163 Hz with a hexagonal-stick single crystal that fits in $0.14 \times 0.21 \times 1.15$ mm$^3$. We

![FIG. 1. (Color online) Temperature dependence of the out-of-plane resistivity $\rho_z$ of $\text{Ag}_5\text{Pb}_2\text{O}_6$ below 70 mK. The sweep rate was approximately 0.05 mK/min. Hysteric behavior at the transition is attributable to a residual magnetic field. The inset photo on the left shows the single crystal used for the measurements. The long axis of the stick corresponds to the $c$ axis. The inset on the right shows the crystal structure of $\text{Ag}_5\text{Pb}_2\text{O}_6$. Red and blue spheres represent the silvers on the Kagome lattice and the chain, respectively.](image-url)
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-diam copper wire on a 0.5-mm-diam polyimide tube (The Furukawa Electric Co., Ltd., PIT-S). The excitation field $H_{ac}$ was 8.7 mOe rms at 887 Hz, which is much lower than the $H_c$ of Ag$_5$Pb$_2$O$_6$. 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 cylinder with a closed bottom, to expel the remaining magnetic flux. The dc magnetic field for the measurements was applied with a small solenoidal coil of Nb-Ti superconducting wire placed inside the shield. The magnitude of the dc field $H_{dc}$ is numerically calculated by taking into account the shielding current on lead shield’s surface.$^{18,19}$

The observed zero-resistivity transition is shown in Fig. 1. A clear zero resistivity is seen, which marks definitive evidence of the superconductivity of Ag$_5$Pb$_2$O$_6$. 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 $\chi'_ac$ of a monocrystal with the magnetic shield described above. 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 Ag$_5$Pb$_2$O$_6$. The measurements were performed under the condition $H_{dc}\parallel H_{ac}\parallel c$. 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 Ag$_5$Pb$_2$O$_6$ 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 $\chi'_ac$ just before the superconducting to normal transitions. These peaks are ascribable to the “differential paramagnetic effect” (DPE),$^{20}$ 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. DPE should be observed in either type-I and type-II superconductors, if pinning of domain walls in the intermediate state of type-I superconductors or of magnetic flux in the mixed state of type II is absent or very weak. However the observed sharp and large DPE near the transition is a hallmark of type-I superconductivity, since $\partial M/\partial H$ in type-II superconductors should be much smaller than 1 near $H_{c2}$ and thus the height of DPE in type-II superconductors cannot exceed $|\chi'_dia|$, where $\chi'_dia$ is the diamagnetic susceptibility in the Meissner state.$^{21}$ We note that preliminary results show supercooling and DPE also for field along the $ab$ plane. Such observation supports that they are intrinsic behavior.$^{22}$

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 superconduct-
Ag$_5$Pb$_2$O$_6$, $H \parallel c$

![Phase diagram of superconducting phase of Ag$_5$Pb$_2$O$_6$, determined from field-sweep data of ac susceptibility.](image)

The residual field has been subtracted in the shield $H_{c0} = 0.040$ Oe from the raw data. The filled squares are the superconducting to normal transition field and should be equal to $H_c$ (see text). The crosses are the supercooling field $H_{sc}$ corresponding to the normal to superconducting transitions. The broken line is the result of fitting with $H_s(T) = H_{c0}[1 - (T/T_{c0})^a]$.

The diagram shows the superconducting transition fields as supercooling fields $H_{sc}$, which is given by $H_{c0}/(1.695\sqrt{2}H_c)$. This gives the upper limit of the GL parameter, which is equal to $1/\sqrt{2}$, the border between type-I and -II superconductors.

This is smaller than the ideal supercooling field $H_{sc,ideal}$, which is equal to $1.695\sqrt{2}k\chi_c$. The observed supercooling field $H_{sc}$ satisfies an inequality $H_{sc} \geq H_{sc,ideal} = 1.695\sqrt{2}k\chi_c$.

Thus, $\kappa$ must be smaller than $\kappa_{sc} = H_{sc}/(1.695\sqrt{2}H_c)$. This 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 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 $\kappa_{sc}$ at $T/T_c \approx 0.9$ 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 $\xi \sim (\xi_0)_{T_c}$, becomes $1.4 \mu$m. This is large enough to cause the size effect near $T_c$ in a sample of $100-200 \mu$m ($\approx 100\xi$).

FIG. 4. The ratio $\kappa_{sc} = H_{sc}/(1.695\sqrt{2}H_c)$ of Ag$_5$Pb$_2$O$_6$, which gives the upper limit of the GL parameter. The upturn of the graph near $T_c$ is attributable to the size effect. The broken line is the result of linear fitting between $T = 35$ and 47 mK, where the size effect is not significant.
metry of Ag$_5$Pb$_2$O$_6$ should be isotropic. The report of this dirty-limit type-I superconductor and thus the pairing symmetry of Ag$_5$Pb$_2$O$_6$ is an oxide type-I superconductor since the discovery of high-$T_c$ cuprates. The ac susceptibility reveals that Ag$_5$Pb$_2$O$_6$ is an oxide type-I superconductor. It is widely considered that type-I 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.

Note added in proof. The band structure reported in Ref. 16 has been substantially revised by a recent calculation and by a recent experiment of quantum oscillations. Nevertheless, the value of $k_F$ used in this paper remains consistent with the recent reports.

We would like to acknowledge K. Ishida, S. Nakatsuji, H. Yaguchi, K. Deguchi, and K. Kitagawa for their support, K. Yamada, R. Ikeda, and S. Fujimoto for helpful discussions, and Y. Sasaki for his advice on experimental techniques. We also appreciate Furukawa Electric Co., Ltd. for providing us with polyimide tubes. This work has been supported by a Grant-in-Aid for the 21st Century COE “Center for Diversity and Universality in Physics” from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan. It has also been supported by Grants-in-Aids for Scientific Research from MEXT and from the Japan Society for the Promotion of Science (JSPS).