Nearly Free Electrons in the Layered Oxide Superconductor $Ag_5Pb_2O_6$

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We present first measurements of quantum oscillations in the layered oxide superconductor $Ag_5Pb_2O_6$. From a detailed angular and temperature dependent study of the de Haas–van Alphen effect we determine the electronic structure and demonstrate that the electron masses are very light, $m^* \sim 1.2m_e$. The Fermi surface we observe is essentially that expected of nearly free electrons—establishing $Ag_5Pb_2O_6$ as the first known example of a monovalent, nearly free electron superconductor at ambient pressure.

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Almost 100 years of low temperature research have established superconductivity as one of nature's favored electronic ground states. The list of superconductors is both long and diverse—multivalent elements [1], complex organic molecules [2], heavy fermion metals [3], and layered oxides [4] are just a few examples of materials in which electrons form a coherent state of Cooper pairs upon cooling. In many of these systems theoretical understanding can be hindered by electronic complexity: even free-electron-like elements such as Al or Pb have a number of bands which cross the Fermi energy E_F, resulting in intricate Fermi surfaces.

It is perhaps the desire to study superconductivity in the simplest environment possible that has driven a long history of exploration in the most primitive of all metallic systems: the ''jellium-like'' alkalis [5–7] and the noble metals Cu, Ag, and Au [8,9]. Despite significant effort, measurements on samples of exceptionally high purity at temperatures in the micro-Kelvin range have yielded no signs of superconductivity. It appeared until now, empirically at least, that nature does not provide us with an example of a single band, monovalent, nearly free electron material that superconducts at ambient pressure [10].

In this Letter we conclude this search by reporting the observation of quantum oscillations in magnetization [the de Haas–van Alphen (dHvA) effect [11]] in the layered oxide superconductor $Ag_5Pb_2O_6$. Our measurements demonstrate for the first time a material that possesses a nearly free electron Fermi surface, *and* superconductivity at low temperatures. In doing so we also resolve a decade old controversy regarding the electronic configuration of this compound, and provide insight into the origins of the unusually large range of observed T^2 resistivity.

$Ag_5Pb_2O_6$ was first grown in the 1950s [12], but it is only in the past few years that single crystal samples have been synthesized [13,14]. The structure of this material is interesting—consisting of planar kagomé lattices of silver atoms separated by PbO_6 octahedra, and threaded with chains of silver atoms along the c axis [15]. Some of us have recently reported bulk superconductivity, with a T_c of

52 mK [16], establishing $Ag_5Pb_2O_6$ as the first example of a layered silver oxide superconductor.

The renewed interest in this system has brought to light a number of outstanding issues. Transport measurements have revealed that the material is a good metal, with a residual resistivity as low as 1.5 and 9.7 $\mu\Omega$ cm for transport within and perpendicular to the planes, respectively. What is very surprising is that the T^2 regime of the resistivity, usually associated with the Fermi liquid state at low temperatures, persists all the way up to room temperature. The pronounced T^2 term leads to a Kadowaki-Woods (KW) ratio that is quite high, about 14 times the usual value of 1.0×10^{-5} $\mu\Omega$ cm $(K\,mol/mJ)^2$ expected in correlated systems [17]. This is particularly unusual as it has been suggested that neither strong electron-electron correlations nor coupling to high frequency optical phonon modes is expected from measurements of the specific heat [14].

Secondly, the origin of metallic transport itself and the electronic structure of the system have proven to be controversial. Jansen *et al.* [15] and Brennan and Burdett [18] have proposed conflicting models of the valence state formulation and electron distribution in $Ag_5Pb_2O_6$, and band structure calculations [18–20] yield strikingly different Fermi surfaces.

To address these issues we used measurements of dHvA oscillations to firmly establish the electronic structure of this material. Our high quality single crystals were grown in Kyoto [14] using a $AgNO_3$ self-flux method with a 5:1 ratio of Ag to Pb. Our samples were rod shaped, approximately 1 mm in length and 50 μm in diameter. The experiments were carried out in a low-noise superconducting magnet system using field sweeps between 15–18 T, at temperatures ranging from 20 mK to 3 K. Detection of the dHvA signal was via a field modulated AC technique. A 6 Hz modulation field of 11 mT in strength was applied and the second harmonic of the voltage of the pickup coils was recorded, essentially providing a measure of $\partial^2 M/\partial B^2$. Two primary dHvA frequencies were observed, and their dependence on the angle between the applied field and the

c axis (the polar angle, θ) is shown in Fig. 1. The alignment of the sample allows for at most a few degrees error in the angular position.

What is immediately obvious from the data is that the high frequency (β) branch is very weakly dependent on θ, indicating extremal electron orbits which do not vary significantly upon rotation. When the field was aligned close to the *c* axis ($\theta = 0$) we observe a second, lower frequency (α) branch, that rises rapidly as θ was increased. No oscillations were observed for $\theta \gtrsim 52°$.

The data in Fig. 1 provide a straightforward test of band structure calculations. Brennan and Burdett [18] have used the extended Hückel implementation of tight-binding theory to compute the electronic structure, and the rather complex Fermi surface they arrive at is reproduced in Fig. 2(c). In their calculations, strong antibonding interactions between silver and the lead oxide octahedra cause the main cylindrical body of the Fermi surface (FS) to splay, with multiple arms radiating along the central plane and extending all the way to the Brillouin zone edges. The predicted dHvA signal would then include contributions from the large electron orbits about the main body of the
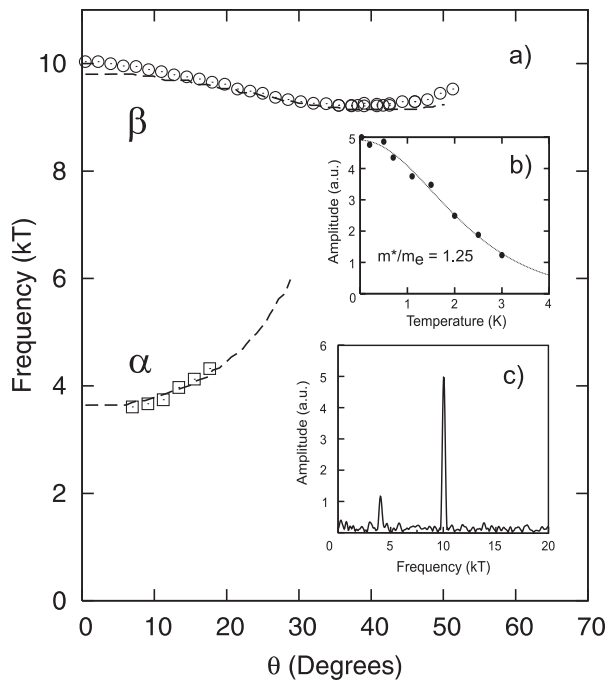
cylinder, with $F \sim 7$ kT on axis, as well as smaller hole orbits between the arms with $F \sim 1.5$ kT on axis.

Our observations clearly contradict this picture. The frequency of the large orbit is some 40% greater than predicted, and its angular dependence does not vary as $1/\cos\theta$ as expected for a cylinder. The smaller frequency is too large to be attributed to the "armpit" hole orbits, and there is no obvious way to account for an orbit of this size. It is apparent then that this initial attempt at band structure calculations completely fails to describe the actual electronic structure of $Ag_5Pb_2O_6$, which is rather unusual given the accuracy such calculations typically have.

The relative simplicity of our results allows us to attempt to reconstruct a plausible FS directly from the data. In the simplest approach, we assume that the electrons are predominantly of nearly free character. Given the carrier density and assuming half filling, the resulting FS is spherical, with radius 0.533 Å^{-1}. Such a sphere would yield a dHvA frequency of 9.34 kT, which already describes our data rather well. The β branch varies by only $\pm 4\%$ upon rotation between 0 to 60°, with an average value of 9.52 kT. As the radius of this sphere is greater than the distance from the midpoint of the Brillouin zone to the c^* axis face, it forms a neck orbit at the top and bottom of the zone, in analogy to the cases of elemental Cu, Au, or Ag. Identifying this orbit with the α branch in Fig. 1 we estimate the neck radius to be 0.322 Å. Combining these two results, an exceedingly simple picture emerges: the Fermi surface is an oblate spheroid with a neck extending along the c^* direction.
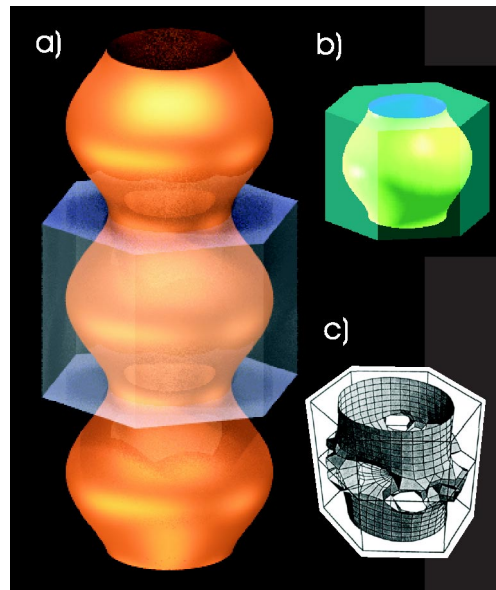

FIG. 1.   (a) Measured dHvA frequencies in $Ag_5Pb_2O_6$ as the angle between the magnetic field and *c* axis is varied. The data for the rotation study was taken at $T \sim 20$ mK and shows two branches labeled α and β. The dashed lines represent dHvA frequencies based on the band structure calculations of Oguchi [20] which predict nearly free electron behavior. (b) The dependence of the amplitude of the β branch at $\theta = 0°$ on temperature. The line through the data is a fit to the standard Lifshitz-Kosevich formula, yielding $m^* = 1.25 \pm 0.10 m_e$. The α branch gives $m^* = 1.1 \pm 0.2 m_e$ for the same orientation (not shown). (c) A sample dHvA spectra taken at $T \sim 20$ mK and $\theta \sim 20°$.

FIG. 2 (color online).   (a) The FS of $Ag_5Pb_2O_6$ as measured by dHvA, shown in the periodic zone scheme, with the translucent box corresponding to the first Brillouin zone of the hexagonal lattice. (b) The FS predicted by the band structure calculations of Oguchi [20]. (c) The proposed FS of Brennan and Burdett [18].

This rudimentary scenario is supported by more recent band structure calculations by Oguchi [20], which predict a half-filled conduction band composed predominantly of Pb-6s and O-2p orbitals with a single nearly free electron per formula unit. The calculated dHvA frequencies in this model are shown by the dashed line in Fig. 1, in remarkable agreement with our data. The convergence of calculation and experimental data is solid evidence that the electronic structure of $Ag_5Pb_2O_6$ is indeed a nearly free-electron-like one.

We may now set about parameterizing the shape of the FS in full detail based on our experimental data. At an arbitrary angle θ, the belly orbit cross section is approximately elliptical with area $\pi k_{min}k_{maj}$ where k_{min} and k_{maj} are the minor and major axes of the ellipse. At $\theta = 0°$, $k_{min} = k_{maj} = 0.552$ Å, and the cross section is a circle. As the sample is rotated, k_{maj} increases while k_{min} remains unchanged, so for a rotation angle θ we can determine k_{maj} from the area of the cyclotron orbit A_c. k_{maj} may then be decomposed into of its in plane (k_x) and out of plane (k_z) components, $k_x = A_c \cos(\theta)/\pi k_{min}$ and $k_z = A_c \sin(\theta)/\pi k_{min}$.

Applying this analysis to both the belly and neck orbits we can then find the dependence of the radius of the FS (k_x) as a function of the distance along the c^* axis (k_z) which may be suitably parameterized in cylindrical harmonics [21]. To a high degree of accuracy, we find that $k_x = 0.444 + 0.112 \cos(k_zc) - 0.005 \cos(2k_zc)$ Å^{-1}, which we use to construct the full three dimensional FS of $Ag_5Pb_2O_6$ in Fig. 2(a). The resemblance to the FS derived from the recent band structure calculations of Oguchi [20], shown in Fig. 2(b), is impressive, confirming the electronic structure of this material.

We may gain further confidence in the validity of this picture by considering the dependence of the experimental signal *amplitude* on angle in Fig. 3. The β-branch oscillations are dramatically enhanced when the field is oriented at angles close to $\theta = 43°$. This effect routinely arises in quasi-2D systems possessing cylindrical Fermi surfaces with a periodic warping along the c axis [22]. For a system with a c-axis lattice constant c, and an average cylinder diameter k_F, such an enhancement is expected at the Yamaji angle, given by $\theta_Y = \arctan(\xi ck_F)$ where $\xi \simeq 2.405$. At this angle, all of the cyclotron orbits about the FS have identical areas, causing a large increase in the signal amplitude. In the present case, the deviation from an ideal cylinder is clearly large, but a remnant Yamaji effect is still expected. Using an average $k_F = 0.437$ Å estimated from the maximum (belly orbit) and minimum (neck orbit) dHvA frequencies, $\theta_Y = 40°$, in good agreement with the peak position in Fig. 3. Additionally, a beating frequency was observed as this angle was approached, which disappeared completely at θ_Y as anticipated in the Yamaji picture.

By analyzing the field dependence of the amplitude of the oscillations we estimate a Dingle temperature of 3.8 K,
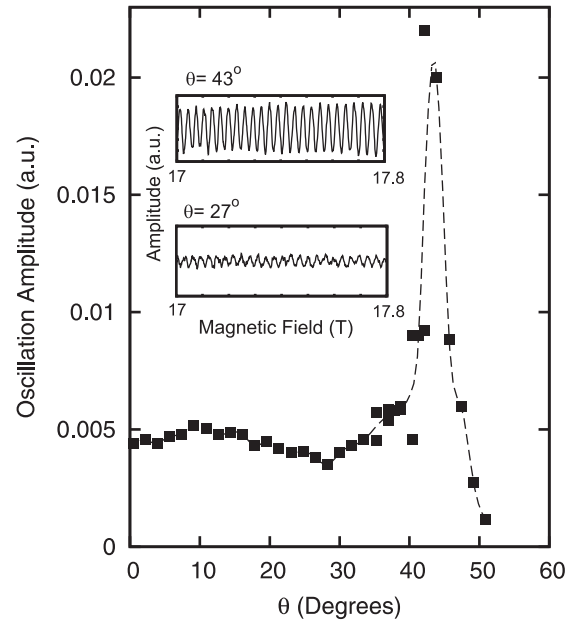

FIG. 3. Main panel: The evolution of the amplitude of dHvA oscillations as a function of polar angle θ. The vertical axis is the Fourier amplitude of the large frequency oscillation, in arbitrary units. Insets: Examples of dHvA field sweeps on $Ag_5Pb_2O_6$, taken for angles $\theta = 27°$ and $43°$. The vertical axis is the pickup signal (in arbitrary units, same scale for both sweeps) at the second harmonic of the excitation frequency. A large enhancement in the oscillation amplitude is seen at the Yamaji angle.

corresponding to a mean free path of 1600 Å. Both figures have an error of ±30%, set by the comparatively low signal-to-noise level in our measurements arising from the small size of our samples.

We have also studied the temperature dependence of the quantum oscillations and find that the effective electron masses are very light. With $B \parallel c$ the standard Lifshitz-Kosevich equation [23] yields $m^* = 1.25 \pm 0.10 m_e$ for the β branch (shown in the inset of Fig. 1) and $m^* = 1.1 \pm 0.2 m_e$ for the α branch. Masses of this magnitude effectively rule out any sizeable electron-electron correlation effects in this system. This number tallies quite well with the observed low-T specific heat, $C_{el}/T = 3.4$ mJ/mol K^2 [14]. Using the free electron approximation above, we estimate $C_{el}/T = \pi^2 m^* k_B^2 N_A/\hbar^2 k_F^2 = 3.85$ mJ/mol K^2 where we have taken $k_F = 0.53$ Å to account for the slightly truncated spherical shape of the Fermi surface. This good agreement implies that there are no additional undetected sheets on the FS.

The very low effective electron mass also implies a small electron-phonon coupling constant. In a simple model, the effect of phonons on electron energy levels within $\hbar \omega_D$ of E_F is to modify the density of states by a factor $1 + \lambda$. This means that in systems with strong electron-phonon coupling the specific heat should deviate considerably from the nearly free electron expectation. The band structure calculations of Oguchi [20] predict a band

mass m_B of $1.2m_e$ for the β branch at $\theta = 0°$, which is identical within error to our measured value of m^*. This implies that λ is exceedingly small, *at most* 0.1, and can thus be taken as strong evidence that the phonons do not play a significant role in renormalizing electronic properties.

The small effective mass also makes the observation of superconductivity in this system rather remarkable [24]. The value of λ in $Ag_5Pb_2O_6$ is, in fact, lower than that observed in other nearly free electron metals. Copper for instance has an $m^* = 1.3m_e$ with $\lambda = 0.3$ for some orbits ([11] and references therein). This is puzzling—if the electron-phonon coupling is so weak in this system, why should $Ag_5Pb_2O_6$ be a superconductor when the noble metals and the alkalis are not?

One intriguing possibility is that the electron-phonon coupling in this system is highly anisotropic, varying significantly in strength as one moves around the Fermi surface. There is evidence that this may indeed be the case from our measurements of the effective mass. The neck orbits are predicted to have an $m_B = 0.68m_e$ when $B \parallel c$ [20], yet the measured mass from dHvA is $1.1 \pm 0.2m_e$ leading to a λ of between 0.3 and 0.9. This is much larger than the λ for the belly orbit, suggesting that perhaps superconductivity arises predominantly from electrons near the necks of the Fermi surface shown in Fig. 2.

These considerations only serve to deepen the mystery of the broad range of T^2 resistivity in $Ag_5Pb_2O_6$. The rather large value of the KW ratio suggests that the T^2 term does not arise from electron-electron correlations in the usual manner, a fact confirmed by our direct measurement of the effective mass.

We speculate that the wide range of quadratic resistivity may be caused by coupling to a series of optical phonon modes, broadly spaced in energy that conspire to produce the observed temperature dependence. This situation is similar to that observed in MgB_2 [25]; however, these modes would have to give a small contribution to the overall phonon density of states, so as to be overlooked by bulk thermodynamic measurements. With the detailed information about the FS geometry presented in this study, a thorough theoretical treatment of electron-phonon coupling in $Ag_5Pb_2O_6$ should be possible. In this respect, a reliable calculation or an experimental measure of the phonon spectrum of this material through infrared absorption or neutron scattering would be extremely valuable.

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