Structural and metal-insulator transitions in ionic liquid-gated Ca$_3$Ru$_2$O$_7$ surface

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We report the fabrication and measurements of ionic liquid gated Hall bar devices prepared on thin Ca$_3$Ru$_2$O$_7$ flakes exfoliated from bulk single crystals that were grown by a floating zone method. Two types of devices with their electrical transport properties dominated by c-axis transport in Type A or that of the in-plane in Type B devices, were prepared. Bulk physical phenomena, including a magnetic transition near 56 K, a structural and metal-insulator transition at a slightly lower temperature, as well as the emergence of a highly unusual metallic state as the temperature is further lowered, were found in both types of devices. However, the Shubnikov-de Haas oscillations were found in Type A but not Type B devices, most likely due to enhanced disorder on the flake surface. Finally, the ionic liquid gating of a Type B device revealed a shift in critical temperature of the structural and metal-insulator transitions, suggesting that such transitions can be tuned by the electric field effect.

The discovery of odd-parity, spin-triplet superconductivity in Sr$_2$RuO$_4$[1] generated much interest in related compounds in the Ruddlesden-Popper (R-P) series of (Ca, Sr)$_n$Ru$_n$O$_{3n+1}$. Interestingly, while strontium ruthenates in the R-P series of Sr$_{n+1}$Ru$_n$O$_{3n+1}$ (Sr$_2$RuO$_4$ is the n = 1 member of the series) are all metals, the calcium ruthenates are more strongly correlated than their strontium ruthenate counterparts, featuring metallic as well as insulating behavior accompanied by magnetic, structural, and metal-insulator phase transitions. In particular, the bilayer calcium ruthenate, Ca$_3$Ru$_2$O$_7$, features a band-dependent Mott metal-insulator transition at 56 K, followed by a structural as well as metal-insulator transition at 48 K as the temperature is lowered.[2,4] Furthermore, a bulk spin valve behavior featuring colossal magnetoresistance was discovered.[5,7] which was attributed to the existence of strongly spin-dependent resistive states in Ca$_3$Ru$_2$O$_7$, which can be tuned by the application of an in-plane field leading to a spin-reorientation and a large resistance change.[6]

Two observations on Ca$_3$Ru$_2$O$_7$ are particularly intriguing. First, despite the co-existence of the structural and metal-insulator transitions at 48 K indicating strong coupling among charge, spin, and lattice degrees of freedom in Ca$_3$Ru$_2$O$_7$, [8,9] resonant X-ray scattering measurements did not yield any evidence for an orbital ordering in Ca$_3$Ru$_2$O$_7$,[10] which raises the question of whether the structural transition is actually electronically driven. Second, a highly unusual metallic state with a very low carrier density was found to emerge below around 8 K. An electronically driven structural transition is a phenomenon of current technological interest in the context of oxide electronics. Similar phenomena was found in vanadium oxide, which features a metal-insulator transition just above room temperature and has been proposed for next-generation field-effect transistor technologies.[11,12] The emergence of an unusually low carrier density metallic state in an insulating phase, which results in the Shubnikov-de Haas oscillations (SdHs), resembles that observed in under doped high $T_c$ superconductors[13] that was attributed to the presence of pre-formed electron pairs. As to the metallic phase found below 8 K, even though its existence was revealed long ago in the flux grown crystals,[2,4] and confirmed in the flux grown crystals more recently,[14] the nature of this phase has rarely been discussed. Electric field effect study of this system will provide insight into these questions.

The challenge of studying the electric field effect of Ca$_3$Ru$_2$O$_7$ is two-fold. First, high-quality thin films of Ca$_3$Ru$_2$O$_7$ are difficult to prepare. Furthermore, Ca$_3$Ru$_2$O$_7$ is neither very resistive or electronically anisotropic, making the non-surface contribution to total sample conductance significant for any electric field effect samples. The exfoliation of layered materials into thin single-crystal flakes, inspired by the graphene work,[15] provides a solution to the first problem. However, the issue of the small surface contribution to total sample conductance is difficult to address. In this regard, making thin flakes and using very high charge density change will help. Specifically, significant electric field effect of Ca$_3$Ru$_2$O$_7$ would require that $10^{13}$-$10^{15}$ cm$^{-2}$ per bilayer be achieved.[16] Ionic liquid gating techniques, capable of inducing up to $10^{15}$ cm$^{-2}$ charge carriers,[17] by the formation of an electrical double layer (EDL) at the sample/liquid interface,[18] have previously been developed for studies of insulating transition metal oxides. Superconductivity was discovered in insulating KTaO$_3$ by gating beyond 3 x $10^{14}$ cm$^{-2}$,[19] and in YBCO the super-
conducting critical temperature was pushed to zero by
depleting a comparable density. EDL gating has also
confirmed carrier-mediation of ferromagnetic ordering in
Ti$_{0.96}$Co$_{0.10}$O$_2$. [21]

Single crystals of Ca$_3$Ru$_2$O$_7$ used in this study were
grown by a floating zone method. Flakes of Ca$_3$Ru$_2$O$_7$
were exfoliated via mechanical cleavage from bulk crys-
tals and deposited onto a substrate of 300 nm SiO$_2$
thermally grown on undoped Si. Flakes are typically on
the order of 30-50 $\mu$m in lateral length, and between
0.5 and 1 $\mu$m in thickness along the $c$-axis; one flake
is shown in Fig. 1a. Thickness was estimated by fo-
cusing the both the flake and the substrate within the
sub-micron depth of view field of our optical microscope,
and confirmed by atomic force microscope (AFM) mea-
surements. We developed a process to contact only
the top surface of the flake by hard-baking a photo-
lithographically defined window on the surface of a flake
before defining metal contacts. We patterned Ti/Au
metal contacts in a Hall bar geometry. A short, low-
power oxygen etch cleaned the sample surface sufficiently
after processing. A completed device is shown in Fig.
1d. This surface-contacted geometry prepares the de-
vice for top-gating with an ionic liquid, shown schemat-
ically in Fig. 1f, and is preferred to maximize the sur-
face signal in metallic, though anisotropic, materials. We
use the ionic liquid N,N-diethyl-N-(2-methoxyethyl)-N-
methylammonium bis(trifluoromethylsulphonyl-imide),
DEME-TFSI) as the gate dielectric. Devices were mea-
sured within a Physical Property Measurement System
(Quantum Design) with a base temperature of 1.8 K and
a 9T superconducting magnet. Gate voltage is applied
just above the freezing point of DEME-TFSI at 210 K[22]
and the sample is cooled with the gate voltage held con-
stant.

In Fig. 2 we show longitudinal resistance $R$ vs. tem-
perature $T$ in two Ca$_3$Ru$_2$O$_7$ flake Hall bar devices. Both
devices showed metallic behavior and essentially a lin-
ear $R \propto T$ behavior until an antiferromagnetic ordering
transition[2, 4] at 54 and 56 K in these two samples, cor-
responding to the 56 K transition in the bulk, resulting in
a sudden drop in sample resistance. Lowering tempera-
ture further, a structural transition and a sharp jump

FIG. 1: (a) Optical image of a Ca$_3$Ru$_2$O$_7$ flake supported
by a Si/SiO$_2$ substrate. Dashed lines outline location of pho-
toresist window to be patterned; (b) Optical image of a device
completed on the same flake with electrical contact made on
the surface of the flake using a window through hard-baked
photoresist; (c) Schematic of the side-view of the device, in-
cluding the coplanar ionic liquid gate (G) setup, with two of
the six contacts acting as source (S) and drain (D).

FIG. 2: (a) Resistance $R$ vs. temperature $T$ in a Ca$_3$Ru$_2$O$_7$
flake with low-$T$ behavior dominated by $c$-axis transport; (b)
d$R$/d$T$ vs. $T$, calculated numerically from (a), highlighting
complex transition behavior at low temperatures; (c) Quot-
ient of the Hall coefficient and thickness $R_H/t$ vs. tempera-
ture $T$ measured at $H = 3$ T in the same device as in (a); (d)
$R$ vs. $T$ in a Ca$_3$Ru$_2$O$_7$ flake with low-$T$ behavior dominated
by $ab$-axis transport; (e) d$R$/d$T$ vs. $T$, calculated numerically
from (d); (f) $R_H/t$ vs. $T$ measured at $H = 3$ T in the same
device as in (d).
in sample resistance was found near 49 and 51 K, respectively, corresponding to the 48 K transition in the bulk [3]. However, qualitatively different behaviors were found for the two devices at low temperatures. For Sample A, the insulating behavior was found below the structure transition, persisting to around 8 K, below which a metallic behavior was found. For Sample B, the insulating behavior lived much shorter than Sample A, with a metallic behavior found below 33 K.

The temperature dependence of the sample resistance seen in Sample A is essentially that of the bulk measured along the c-axis, $\rho_c$, while that seen Sample B, resembles that of the bulk in-plane resistivity, $\rho_{ab}$. [7, 14, 23] The c-axis resistivity of the bulk crystals was found to feature more than a factor of eight resistance rise below the structural transition in bulk crystals, and that for our Sample A is roughly factor of 4, which suggests that the sample resistance measured in Sample A contains contributions from both ab- and c-axis electrical transport. Interestingly, the temperature dependence of the sample resistance for Sample A, which we refer here to as a Type A sample, was found in most devices we prepared. Given that the ratio of c-axis resistivity $\rho_c$ to ab-axis resistivity $\rho_{ab}$ is only over factor of three, this is not unexpected. Devices with behavior resembling to that of Sample B, which we refer to as a Type B sample, were much harder to come by. The sample resistance for Type B samples consists mostly contribution from the flake surface, taking up the behavior of bulk $\rho_{ab}(T)$.

The feature found at 33 K in bulk $\rho_{ab}$ [23], which was seen in $R$ vs. $T$ for Sample B and in $dR/dT$ for Sample A, marks the onset of a quasi two-dimensional metallic state. The metallic behavior found in $\rho_c$, below 8 K, on the other hand, signals a incoherent-coherent transition in the c-axis transport and the emergence of a fully three-dimensional metal in Ca$_3$Ru$_2$O$_7$. Interestingly, the 8 K feature in $\rho_c$ was observed in floating zone [14] but not in self-flux grown crystals. [7, 23] which seems to suggests that coherent c-axis transport is fragile, sensitive to disorder. The observation of the 8 K feature in our Type A sample therefore suggests that the good crystallinity of our flakes, consistent with the temperature dependence of the Hall coefficient, $R_H(T)$, shown in Fig. 2c. Incidentally, small deviation from bulk behavior in $R_H(T)$ was found for Sample B at low temperatures, likely reflecting the effect of disorder on the flake surface.

The above analysis is supported by our observation of SdHOs in Type A samples which are absent in Type B samples. We show in Fig. 3a $R$ with $H$ at $T = 1.8$ K in a Type A device. The background-subtracted resistance oscillations, $\Delta R$ vs. $H^{-1}$, were shown in Fig. 3c. Similar behavior was found in a separate Type A device (data not shown). Up to three sets of oscillations were observed in bulk Ca$_3$Ru$_2$O$_7$. [14, 23] However, a Fourier transform of $\Delta R$ obtained in our flake devices suggests only a single set of SdHOs with a frequency of 43 T, which was also seen in the bulk, likely due to a low maximum $H$ in the present work. It is known that the frequency of SdHOs depends on the carrier density. Even though the precise carrier density of the device cannot be obtained from the Hall measurements because the thickness of the layer affected by the gating is not known, the carriers added to the surface can be estimated based on our control experiment carried out on graphene. Careful comparison of the SdHOs without gating with those obtained when a ionic liquid gating voltage of 3 V was applied, corresponding a carrier density change larger than 10$^{13}$ cm$^{-2}$, the SdHOs remained essentially the same (Figs. 3b and d). This observation suggests that the SdHOs can not come from the surface of the flake. Incidentally, SdHOs were not observed in Type B samples, which, together with the deviation from the bulk behavior seen in $R_H(T)$, indicates clearly that the transport in Type B samples is dominated by the surface layer featuring disorder stronger than that in the interior of the flake. The surface dominance in Type B samples could be due to mechanical separation formed during the exfoliation process even though there is no direct evidence for it.

The surface layer-dominated transport in Type B samples facilitates measurable response to applied gate voltage $V_G$ across an ionic liquid. In Fig. 3b, we show that with $V_G = 3$ V, the induction of electrons at the flake surface increases conductivity by up to 20% at lowest temperatures in the metallic regime, likely due to an added carrier density larger than 10$^{13}$ cm$^{-2}$ as men-
FIG. 4: (a) Resistance $R$ vs. temperature $T$ in a Ca$_3$Ru$_2$O$_7$ flake whose electrical transport is dominated by $ab$-axis transport, for zero and finite applied gate voltage $V_G$; (b) $dR/dT$ vs. $T$ calculated numerically from (a).

that the onset temperature for this metallic state with a tiny carrier density appears to be unchanged under a 3V ionic liquid gating. Together with the fact that the 56 K magnetic transition was barely shifted by the same ionic liquid gating of 3 V, our experiment seems to suggest that the emergence of this metallic phase is magnetic in origin.

In conclusion, we have developed a surface-contact technique for devices prepared on exfoliated Ca$_3$Ru$_2$O$_7$ flakes. Comparison with features seen on these devices prepared on exfoliated Ca$_3$Ru$_2$O$_7$ flakes and those in floating zone-grown bulk crystals suggests that the transport properties observed in the Type A and Type B samples are dominated by $c$ axis and in-plane contributions, respectively. Magneto electrical transport measurements, including the observation of SdHOs, support the emergence of a highly unusual metallic state featuring small Fermi surface pockets at low temperatures. The demonstration of an electric field effect on the structural transition temperature on Ca$_3$Ru$_2$O$_7$ surface suggests a new approach to the study of complex transition metal oxides for which thin films are unavailable.

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