Atomically thin sheets of the layered honeycomb magnet SrRu$_2$O$_6$ by liquid exfoliation

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The room temperature magnet SrRu$_2$O$_6$, is endowed with a quasi-two-dimensional layered structure like graphene, comprising of a Ru-honeycomb lattice separated by alternate Sr layers. However, unlike graphene, the honeycomb is magnetic - consisting of the 4$d$ Ru ions with strong spin orbit coupling. This, together with inherent antiferromagnetic correlations on a hexagonal lattice makes SrRu$_2$O$_6$ a prime candidate for exploring novel quantum states of matter. Here we report the synthesis and characterization of atomically thin sheets of SrRu$_2$O$_6$, obtained using liquid exfoliation - a technique primarily meant for scalable exfoliation of Van der Waals driven layered systems. These nano-sheets dispersed and preserved in ethanol and drop-cast on suitable substrates are characterized by Scanning Electron and Transmission Electron Microscopy. Electron diffraction patterns exhibit hexagonal symmetry of the underlying lattice, confirming the crystallinity of nano sheets and suggest that these sheets are primarily exfoliated from a plane perpendicular to the Ru-honeycomb. Atomic Force Microscopy confirms that the average thickness of nano sheets fall in the range of 2 to 3 monolayers. The nano-sheets thus obtained offers the possibility of fabricating devices based on this important quantum material.

I. INTRODUCTION

Strongly correlated electron systems - where electronic correlations manifest itself in the form of new and emergent quantum co-operative phenomena - continues to occupy a prominent position in condensed matter physics. The 3$d$ transition metal oxides are prime candidates in the area of strongly correlated electron systems, as exotic electronic states like high temperature superconductivity, colossal magnetoresistance, multiferroicity, charge and orbital ordering have been unearthed in these systems[1, 2]. The electronic properties in these materials are primarily dictated by the competition between the on-site Coulomb repulsion and the electron band-width. Materials where these two competing energy scales have similar magnitudes are especially interesting. This scenario has drastically changed in the past decade or so, with a host of novel electronic and magnetic ground states being realized in the 4$d$ and 5$d$ transition metal oxides, arising from relativistic Spin Orbit Coupling (SOC) which is much higher than the 3$d$ based compounds [1].

The primary bottleneck which prevents the use of these 4$d$ and 5$d$ transition metal oxides in the next generation of multifunctional devices, is that the transition temperatures of most of these oxides are far below room temperature. Hence, the realization of strongly correlated oxides with high transition temperatures is an area of intense theoretical and experimental investigations. In this context, the recent discovery of a high magnetic ordering temperature in the environmentally benign SrRu$_2$O$_6$ which possess $T_N$ of the order of 560K is of great importance[3–13].

SrRu$_2$O$_6$ crystallizes in an inherently layered structure, with a graphene-like magnetic hexagon comprising of Ru$^{3+}$ ions. Strongly correlated electrons stabilizing in hexagonal structures with antiferromagnetic (AFM) interactions provide a fertile playground for hosting unconventional excitations[14–17]. For instance, SrRu$_2$O$_6$ has been predicted to host a strain mediated topological states [3–6], with such strain being realized by a number of potential ways including externally applied pressure or doping. The fact that none of these approaches have been experimentally tried out as yet, makes this an area with immense promise, both from the viewpoint of fundamental physics, as well as potential multifunctional devices. Furthermore, SrRu$_2$O$_6$ is predicted to possess some exotic electronic properties owing to both localized and itinerant character of electrons in benzene-like rings comprising of Ru hexagon. Here, due to the possibility of electronic conduction from direct Ru-Ru hopping as well as Ru-oxygen hybridized states this system is predicted to host novel Quantum Spin Liquid (QSL) states [10, 18–20]. In this context, SrRu$_2$O$_6$ is quite similar to the celebrated RuCl$_3$ and Na$_2$IrO$_3$ systems, which have been explored for hosting fractionalized Kitaev physics with unconventional excitations [13, 21–25].

In the present work we report the synthesis of atomically thin sheets of SrRu$_2$O$_6$ by a scalable technique of liquid exfoliation. These nano sheets are formed and preserved in the liquid medium, ethanol, which enables their drop casting on a suitable substrate for further characterization and device patterning. Obtaining this important quantum magnet in the form of ultra thin sheets may lead to novel electronic and magnetic states in this compound, and therefore adds an important addition in the family of 2D materials [26–30]. Experimental realization of graphene-like magnetic oxides is a relatively less explored area, especially considering the fact that SrRu$_2$O$_6$ is a room temperature magnet with strong spin orbit coupling. The paper is organized as follows. We first discuss the characterization of bulk SrRu$_2$O$_6$, followed by a brief discussion on the liquid exfoliation technique and experimental parameters involved in obtaining the nano sheets using this compound. 

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Figure 1. (a) Structure of SrRu$_2$O$_6$ depicting the honeycomb lattice of Ru ions (gray balls) within the $ab$ plane. The Ru layers are separated by Sr layers (green balls) along the $c$ axis. (b) shows the room temperature powder XRD data for SrRu$_2$O$_6$ formed using hydrothermal synthesis. Here the intensity has been normalized with the most intense peak of SrRu$_2$O$_6$. A tiny impurity of RuO$_2$ has been marked by stars in the figure, whereas the remaining peaks correspond to the pure SrRu$_2$O$_6$ phase. (c) shows the Raman data, obtained on a crystallite of SrRu$_2$O$_6$. (d) is the optical image for the crystallite shown in the inset. The morphology of the sample is depicted in the SEM image of bulk SrRu$_2$O$_6$ as shown in (d), which depicts overall view of micron-size crystallites forming in regular morphology. (e) and (f) are images of isolated hexagonal crystallites and regular polyhedra. The liquid exfoliation technique has been employed to obtain atomically thin sheets of SrRu$_2$O$_6$, using these regular shaped crystallites shown in (d) to (f).

Finally we present the characterization data including SEM, TEM and AFM on the nano sheets of SrRu$_2$O$_6$ thus formed.

II. EXPERIMENTAL TECHNIQUES

SrRu$_2$O$_6$ crystallites are synthesized via the hydrothermal route, using an autoclave from Parr instruments. The raw materials KRuO$_4$ and SrO$_2$, were procured from Alfa Aesar and Sigma Aldrich respectively. The morphology and size of as synthesized bulk crystallites as well as nano-sheets are recorded using a Zeiss Ultra plus FESEM. Powder X-ray diffraction (XRD) on the crystallites have been conducted using Bruker D8 Advance with Cu K$_\alpha$ radiation ($\lambda = 1.54056$ Å). Raman spectroscopy has been done using Horiba instruments equipped with a blue laser($\lambda = 488$ nm) and a confocal microscope. The nano sheets are further characterized using Transmission Electron Microscopy (TEM) FEI-TECNAI microscope and Atomic Force Microscopy (AFM) using JPK Nanowizard II.

A. Liquid Exfoliation Technique

The process of liquid exfoliation has been employed to form atomically thin sheets of graphene-like Van der Waals materials of technological importance including a wide variety of chalcogenides such as MoS$_2$ [31–34]. This process involves finding a suitable liquid medium in which the bulk sample is sonicated and centrifuged. Here important synthesis parameters include (i) sonication which enables separation of layers which are weakly bonded (ii) centrifugation which enables isolation of thin sheets. The suitable choice of liquid medium or solvent is important, as it prevents the isolated nano sheets from coagulating again. Time of sonication and centrifugation are also crucial parameters that can be tuned to further refine the thickness distribution as well as size of the nano sheets[31–34]. While a large number of layered Van der Waals materials have been successfully exfoliated using this technique, there are relatively few reports (ref) of exfoliation of layered magnetic oxides using this technique. Oxides such as SrRu$_2$O$_6$ are quasi two dimensional in the sense of weak interlayer bonding as compared to in-plane bonding, though both inter-plane and intra-layer bondings are co-valent in nature. Through the weakly bonded layer (which is the Sr layer in this particular case) the nano sheets of not only SrRu$_2$O$_6$ could be exfoliated, as demonstrated in this work, but also we have successfully exfoliated some other magnetic oxides, which are not Van der Waals driven, but possess layered structure (not shown here).

III. RESULTS AND DISCUSSIONS

A. Synthesis and characterization of SrRu$_2$O$_6$ crystallites

The compound SrRu$_2$O$_6$, crystallizes in a quasi-2D structure with space group $P - 31m$ and lattice parameters $a = 0.520573$ nm, $c = 0.523454$ nm [3]. As shown in Figure 1a, the structure of SrRu$_2$O$_6$ comprises of edge-sharing RuO$_6$ layers separated by Sr$^{2+}$ ions. Within the $ab$ plane, the Ru ions are arranged in a honeycomb structure and Ru moments couple antiferromagnetically both in-plane and out-of-plane. The magnetic moment is $1.30 \mu_B$/Ru at room temperature and the system possesses the G-type magnetic structure[3, 4]. For obtaining the nano sheets, we first synthesize bulk SrRu$_2$O$_6$
employing the hydrothermal technique described by Hiley et al. [3]. For this purpose, KRuO₃ and SrO₂ (in stoichiometric ratios) are added in distilled water and stirred, prior to heating the mixture 200°C for 24 hours in an autoclave. The precipitate was recovered using a vacuum filtration assembly and washed with diluted HCl, distilled water and acetone. The sample thus obtained was characterized by XRD, as is shown in Figure 1b and Figure 1c respectively. The XRD pattern matches well with, JCPDS[04-021-3995] entry assigned for SrRu₂O₆[3]. A tiny amount of RuO₂ phase is also observed as marked by stars in Figure 1b, for which the peaks match with JCPDS[65-2824]. This impurity could be systematically reduced by repeated washing the as-prepared compound (Supt. Info-Text-S1 and Figure S1). A characteristic Raman spectra acquired using blue laser is shown in Figure 1c. The optical image of a crystallite, on which the Raman data has been recorded is shown in the inset of Figure 1c. The Raman active modes are consistent with the previous reports[12]. The morphology of the SrRu₂O₆ crystallites is shown in Figure 1d-1f. Here Micron-size crystallites are observed with regular facets, vertices and edges as depicted in Figure 1d-1f. A large number of crystallites are formed in regular hexagonal shape as is highlighted in Figure 1e. The bulk SrRu₂O₆ sample has also characterized using synchrotron XRD as a function of temperature. A representative data recorded at 100 K shown as a Supp. Info. Figure S2. The lattice parameters, obtained using Rietveld Profile refinement of XRD data are consistent with previous reports [3, 4].

B. Synthesis and Characterization of nano sheets : SEM, AFM and TEM

To obtain nano sheets of SrRu₂O₆, the first task is to determine a suitable solvent or a liquid medium, in which the bulk crystallites can be dispersed. This solution is then subjected to sonication for mechanically isolating the weakly bonded layers. After trying a number of solvents, we found that ethanol is most suitable for obtaining atomically thin sheets of SrRu₂O₆. This also enables an easy means to drop cast these sheets on a suitable substrate for further processing, as ethanol evaporates and enables easy device patterning. In order to synthesize atomically thin sheets, we first make a solution of SrRu₂O₆ crystallites in ethanol in 1:10 ratio. This solution is subjected to 4 hours of bath and probe sonication, following which the solution is kept undisturbed for 24 hours. The top portion of the solution is collected and centrifuged at 2000 rpm for 30 minutes. The centrifuge vial is kept undisturbed, prior to retrieving a few µL from the top layer using a micro pipet. This solution is then drop-casted onto the various suitable substrates for further characterization.

Figure 2a-2d displays SEM images of nano sheets thus formed. The images are recorded by drop-casting the dispersed nano sheets on a Si substrate. As evident from Figure 2, the sheets are formed in various shapes and size, for which a few representatives are shown here. Most importantly, we observe a significant fraction of sheets retain the shape of regular polyhedra of as-formed micro-crystals shown in Figure 1b. Both isolated as well a bunch of sheets (which lie on top of each other) can be found. The lateral length of such nano sheets varied from few tens of nano meters to a few tens to a few hundred nm and again appears to correlate with dimensions of the bulk SrRu₂O₆ crystallites, from which these sheets have been exfoliated.

While the wide variety in the relative thickness of the sheets can be gauged from the contrast in the SEM images, we performed AFM measurements for determining the average thickness of the nano sheets. For this purpose, a few µL of the solution is drop-cast on a freshly cleaved mica substrate. Figure 3a-d shows some representative AFM images on the nano sheets of SrRu₂O₆. Figure 3a shows a broad area AFM image, displaying a large number of sheets of various shape and size on the substrate. This also demonstrates the scalability factor which the technique of liquid exfoliation provides. This is especially relevant in this particular case, as Density Functional Theory (DFT) calculations have suggested that the strain mediated topological properties could be observed in samples with certain thickness[6]. It is evident that a large number of isolated sheets with various thickness provide a
means to pick the sheets with desired thickness for future magnetotransport measurements. From AFM images shown in Figure 3b, we find that many of these nano sheets retain the hexagonal shape of the bulk crystallites. This is evident from Figure 3b-d, which shows a neatly formed hexagonal sheet, a rather distorted hexagon and also a fairly arbitrary shape sheet. The average thickness of most sheets range from 2 to 3 monolayers stacked perfectly. We found that after step 1 and step 2, the vial containing sheets basically forms a density gradient, which needs to be kept undisturbed for a long time (preferably a few hours), before taking out the requisite sample for drop-casting on substrate for characterization.

Further to this, we observed that repeating the entire process of sonication and centrifugation (after leaving the dispersed nano sheets for months in the vial) resulted in narrower distribution of thickness, as compared to the case when the sample is repeatedly taken from the same vial. In all these samples, many regions with partially stacked sheets could also be found. Thus it is evident that the each step involved in the process of liquid exfoliation, including the time of sonication and centrifuge can be further refined to obtain either monolayers or stacked layers or partially stacked sheets. We emphasize that each of these patterns are interesting for exploring the topological states in 2D materials in general, [35–37], and more so in the case of SrRu$_2$O$_6$, wherein DFT predicts strain mediated topological state and band inversion, when c axis in the unit cell could be significantly tailored, while and other two lattice parameters remain relatively unchanged [6]. It is evident here that the nano sheets of SrRu$_2$O$_6$ produced using the technique of liquid exfoliation possibly provides a means to obtain atomically thin 2D sheets, in which a particular lattice parameter (perpendicular to the weakly bonded layers) can be tuned significantly, without much disturbing the other two (in-plane) lattice parameters. Moreover, ease in finding multiple layers with different stacking number can enable one to experimentally test these predictions[6].

The crystalline nature of the atomically thin sheets is further confirmed by high resolution TEM images as shown in Figure 4. Here a few µL of SrRu$_2$O$_6$ nano sheets dispersed and preserved in ethanol solution are drop cast on a TEM grid. A representative low resolution bright field image is shown in Figure 4a, depicting a portion of a typical folded sheet of SrRu$_2$O$_6$, which is about 100 nm wide and a few 100 nm long. The electron diffraction spots obtained from different areas of this sheet are shown in the bottom of Figure 4a, depicting Bragg spots in a hexagonal pattern. These Bragg spots confirms the crystallinity of the nano sheet and also suggests that the sheets have been exfoliated from a plane, which is perpendicular to the plane containing the Ru$^{5+}$-Hexagon. The crystallinity of the nano sheets can also be gauged from a high resolution image shown in Figure 4b, depicting the well formed lattice planes. The corresponding ED pattern is shown in the inset. On closer inspection, a lot of nano-sheets were found to have displaced staking as well as folding, a representative of which is shown in Figure 4c with a buckled structure, highlighted by a yellow marker. Figure 4d shows another isolated sheet, in which the FFT on a selected area showed ED with hexagonal symmetry.

Over all these TEM and AFM images illustrate that various type of nano sheets of SrRu$_2$O$_6$ can be easily formed using liquid exfoliation and drop-cast on any patterned substrate for electron-transport or magnetic characterization. When drop-cast on a suitable substrate, it should be possible to explore novel electric properties [26–28] of these magnetic nano sheets.

**IV. CONCLUSION**

In conclusion, we demonstrate the successful exfoliation of a layered magnetic oxide with a magnetic honeycomb lattice consisting of heavy ion Ru, with strong spin orbit coupling.
Figure 4. (a) shows a broad area TEM image, depicting a folded nano-sheet of SrRu$_2$O$_6$. The corresponding electron diffraction patterns obtained from a selected area of this folded sheet are shown at bottom of (a). The underlying hexagonal symmetry, revealed from the electron diffraction patterns indicates that the sample is exfoliated in the direction which is perpendicular to the plane containing the Ru hexagon. (b) is a high resolution TEM image depicting the lattice planes of SrRu$_2$O$_6$, with the corresponding diffraction pattern of a selected area of this sheet shown as inset. (c) shows a broad area TEM image, depicting a buckled pattern as observed in part of the nano sheet, highlighted in the yellow square. (d) shows a different SrRu$_2$O$_6$ nano sheet and the associated FFT image.

The electronic structure of SrRu$_2$O$_6$ maps on to a benzene molecule like molecular orbit with both itinerant and localized character of electrons. While the method of liquid exfoliation is primarily meant for Van der Waals materials, we show that the same technique can be successfully employed to obtain nano sheets of layered magnetic oxides such as SrRu$_2$O$_6$, which possess weakly bonded layers in a particular direction. Scanning and Transmission electron microscopy as well as Atomic force microscopy confirm that these nano-sheets were also obtained in regular hexagonal shape, reflecting the underlying symmetry of the magnetic Ru$^{5+}$ hexagon. These atomically thin sheets, formed using this scalable technique can be easily drop-cast on suitable substrates for characterization as well as on patterned substrates for magnetotransport measurements. These graphene-like sheets of SrRu$_2$O$_6$ provides a means to retain the in-plane antiferromagnetic interactions and reduce the perpendicular ones, which leads to the possibility of experimentally realizing the exotic strain mediated topological properties which this compound is predicted to possess.

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