Electronic Excitations and Structure of Heteroepitaxial Li$_2$IrO$_3$ Thin Films

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Thin films are a prerequisite for application of the emergent exotic ground states in iridates that result from the interplay of strong spin-orbit coupling and electronic correlations. We report on pulsed laser deposition of heteroepitaxial Li$_2$IrO$_3$ films on ZrO$_2$:Y(001) single crystalline substrates. X-ray diffraction confirms a preferential (001) out-of-plane crystalline orientation with a defined in-plane epitaxial relationship. Resistivity between 35 and 300 K is dominated by a three-dimensional variable range hopping mechanism. The dielectric function is determined by means of spectroscopic ellipsometry and, complemented by Fourier transform infrared transmission spectroscopy, reveals a small optical gap of $\approx 300$ meV, a splitting of the $5d$-$t_{2g}$ manifold, and several in-gap excitations attributed to phonons and possibly magnons.

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The layered perovskite oxides A$_2$IrO$_3$ (A = Na, Li) have in recent years been studied in terms of a physical realization of the Kitaev and Heisenberg-Kitaev model and its extensions, harboring spin liquid and topologically ordered phases. They have also drawn interest as possible topological insulators. Ultimately, the physical realization of such states of matter is desired with respect to quantum computation proposals. Subsequently, experiments showed that both materials order magnetically at $\approx 15$ K: Na$_2$IrO$_3$ is deep within an antiferromagnetically zig-zag ordered phase, whereas Li$_2$IrO$_3$ shows incommensurate spiral order but is placed close to the desired spin liquid phase. There is yet no direct experimental evidence of a topological insulator phase in either of the two materials. However, theoretical studies predict that a topological insulator phase can be achieved by application of strain.

Some of us have previously reported on the first successful growth of heteroepitaxial Na$_2$IrO$_3$ thin films, where we observed three-dimensional variable range hopping conductivity and the weak antilocalization effect in magnetoresistance. To date, available single crystals are of very small size, such that experimental data on Li$_2$IrO$_3$ is often restricted to powder-averaged data or polycrystalline samples. Certain types of experiments, such as terahertz pump-probe spectroscopy or neutron diffraction, benefit from large-area single-crystalline thin film samples. Neutron diffraction experiments, for instance, are challenging because of a high absorption cross-section if iridium and the small crystal sizes. Thin films however alleviate these problems by distributing the volume over a large area. In addition, epitaxial thin films allow the incorporation of strain and the study of its effects and generally pave the way for future device applications. In fact, it is believed that the application of c-axis pressure can bring Li$_2$IrO$_3$ even closer to the spin liquid phase. Hence, thin films of this class of material lay a foundation for future experiments including e.g. studies on the (Na$_{1-x}$Li$_x$)$_2$IrO$_3$ compounds, which are not available in single crystalline form so far.

Like its sister compound Na$_2$IrO$_3$, Li$_2$IrO$_3$ is an antiferromagnetic insulator with Néel temperature $T_N \approx 15$ K below which it orders in an incommensurate spiral fashion. X-ray powder diffraction measurements suggest a monoclinic C2/c unit cell. Temperature dependent resistivity shows insulating behavior between 100 and 300 K. A delicate interplay between trigonal distortions of the IrO$_6$ octaeder and spin-orbit coupling cause the spin-orbit assisted Mott insulating state. Until recently, the magnitude of the trigonal distortions was unclear. Consequently, the adequate description of the underlying electronic structure was under debate. However, recent resonant inelastic x-ray scattering experiments validate the applicability of the so-called $j_{\text{eff}}$ physics in Li$_2$IrO$_3$, which in the past was applied to Sr$_2$IrO$_4$ and related materials. The cubic crystal field caused by the edge-sharing IrO$_6$ octaeder splits the Ir $5d$ orbitals into a $e_g$ doublet and a $t_{2g}$ triplet. The splitting between $e_g$ and $t_{2g}$ is about 3 eV. Structural distortions of the monoclinic unit cell and the oxygen tetraeder, respectively create a trigonal crystal field. If this field is sufficiently small compared to spin-orbit coupling, the $t_{2g}$ triplet further splits into a fourfold degenerate $j_{\text{eff}} = 3/2$ and a twofold degenerate $j_{\text{eff}} = 1/2$ band.

In this paper, we report on the pulsed laser-deposition of heteroepitaxial Li$_2$IrO$_3$ thin films. Temperature-dependent resistivity is measured between 300 and 25 K. Employing spectroscopic ellipsometry, we determine the dielectric function in order to study and interpret low energy electronic excitations on the basis of $j_{\text{eff}}$ physics. These results are complemented with optical transmission data measured with a Fourier transform infrared spectrometer.

Heteroepitaxial thin films were grown by pulsed laser
depositon (PLD) on 10 × 10 mm² ZrO₂:Y(001) single crystals (YSZ) at a temperature and oxygen partial pressure of 600°C and 3.0 × 10⁻⁴ mbar, respectively. PLD was done with a 248 nm KrF excimer laser at a laser fluence of 2 J cm⁻². The phase-pure polycrystalline target was prepared by a solid state synthesis of Li₂CO₃ and IrO₂ powders in a stoichiometric ratio of 1:1:1.

Investigations of the epitaxial relationship were performed with both a Panalytical X’Pert PRO MRD with PIXcel³D detector and a Philips X’Pert x-ray diffractometer equipped with a Bragg-Brentano powder goniometer using divergent/focusing slit optics and Cu Kα radiation. Surface morphology was investigated via a PARK System XE-150 atomic force microscope in dynamic non-contact mode and a CamScan CS44 scanning electron microscope. Temperature dependent dc electrical resistivity was measured in van-der-Pauw geometry with dc magnetron-sputtered ohmic gold contacts. The dielectric function (DF) was determined via standard variable angle spectroscopic ellipsometry in the spectral range from 0.03 to 3.34 eV. Infrared optical transmission in the spectral range from 0.14 to 1.30 eV was measured using a BRUKER IFS 66v/S Fourier transform infrared spectrometer in transmission mode (T-FTIR).

The x-ray diffraction (XRD) 2Θ-ω pattern of a Li₂IrO₃ film is shown in Fig. 1(a). The pattern is indexed on the basis of a monoclinic C2/c unit cell [3] [13]. The pattern shows pronounced symmetric peaks related to the (001) planes of the Li₂IrO₃ phase, thus indicating an out-of-plane preferential orientation. Two minor additional reflections, with intensities below 20 cps, likely relate to the (220) and (440) planes [denoted as * in Fig. 1(a)]. From the peak positions of the (002), (004) and (006) reflexes, the out-of-plane lattice parameter c is determined as 9.835 Å. It is in excellent agreement with reported values. [3] [19] The in-plane lattice parameters could not be determined due to insufficient intensities of the respective reflexes. However, because of the large lattice mismatch between substrate and film a relaxed growth without any strain is assumed.

Investigation of the in-plane epitaxial relationship is done by high-resolution x-ray diffraction φ-scans of the asymmetric Li₂IrO₃ (131) and YSZ (111) reflections, shown in Fig. 1(b). For YSZ(001), we observe the Cₛ-symmetry of its (111) planes as expected. The φ-scan of the Li₂IrO₃ (131) reflection shows 24 reflections spaced by 15° alternating between “high” and “low” intensity. This indicates that the Cₛ-symmetric (monoclinic) (001)-oriented Li₂IrO₃ epilayer aligns in-plane within 24 rotational domains. The domain ratio is approximately 7:1. From the mismatch of rotational symmetry of substrate and epilayer, [30] we expect a minimum of four rotational domains. The origin of the increased number of rotational domains is at present unknown. One explanation might however be possible: Initially, Li₂IrO₃ was reported as pseudo-hexagonal. [20] If it occurred, the (co-)existence of epitaxially induced Cₛ-symmetry would lead, according to Ref. [30], to two rotational domains and thus 12 reflections in total. Adding the possibility of a Zr-/O-terminated YSZ-surface, the number of reflections further increases to 24. Based on our x-ray data, it is not possible to determine the actual crystal structure of the epilayer, as the (001) planes of both monoclinic and pseudo-hexagonal symmetries share similar 2Θ angles. Epitaxially induced change of lattice symmetry was e.g. observed for the growth of U₃O₈ on c-plane Al₂O₃. [31]

Figures 1(c,d) show topographic images of the Li₂IrO₃ film surface obtained with scanning electron microscopy (SEM) and non-contact atomic force microscopy (AFM), respectively. The images reveal a columnar surface structure with an RMS roughness of 15.7 nm and a peak-to-valley height of 139.0 nm. The relatively high surface roughness might be explained by the large number of rotational domains, as observed in XRD (cf. 1(b)).

As illustrated in Fig. 2 Li₂IrO₃ exhibits semiconducting resistivity behavior between 300 and 25 K which does not follow a simple activated law. Instead, resistivity is dominated by three-dimensional Mott variable range hopping down to at least 60 K, as similarly observed in Na₂IrO₃ thin films. [19] At lower temperatures, resistivity diverges steeply to higher values.

Spectra of the DF were determined from the ellipsometry data by using a model containing a layer for the substrate, a layer for the Li₂IrO₃ film and a surface roughness layer. Each layer is described by its thickness and optical constants. Between the substrate and the Li₂IrO₃ thin film, a thin interface layer of about 1 nm was introduced by mixing 50:50 the substrate and film DF in a ratio of 1:1 by means of a Bruggeman effective-medium approximation (EMA). [32] Also the surface roughness...
layer and the columnar structure was accounted for by a 100 nm EMA-layer by mixing the film DF with void. The void fraction was gradually increased from ~20 to ~80% from bottom to top (please cf. note [33]). For modelling the thin film’s DF we used a parametric model dielectric function (MDF) approach consisting of (cf. Fig. 3): a Drude free charge carrier absorption and two Lorentzians describing the phonon contribution at lowest energies; a near band gap Tauc-Lorentz (TcLo) absorption function [34] and a series of M0-critical point functions with parabolic onset [35] [36] describing direct band-band transitions; Gaussian oscillators were used to model electronic band-band transitions spread within the Brillouin zone at higher energies. Additional discrete transitions where described by Lorentzians. Regression analysis was then applied to best match the dielectric function model to the experimental data. From the MDF, the absorption coefficient α was calculated (cf. Fig. 3).

The final MDF together with its individual components is displayed in Fig. 3. In the following, we argue that these individual components represent electronic excitations in line with the picture of j_{eff} physics and other reported experimental results. The observed excitations are summarized in Table I. In the high-energy spectral range above 1.2 eV, we find two contributions to the MDF at 1.63 and 3.25 eV that are attributed to d-d band transitions from occupied t_{2g} to empty e_{g} bands (D, E). Very similar transitions have been observed in Na_{2}IrO_{3} and Li_{2}IrO_{3} single crystals [21] [37] and Na_{2}IrO_{3} thin films. [19] Below 1.2 eV, we find several transitions. The transitions at 55 and 65 meV are attributed to phonons; at 0.11 and 0.18 eV we find discrete transitions (A). For example, in Sr_{2}IrO_{4} a magnon was found at 0.2 eV within the Mott gap. [35] Further band-band excitations, possibly related to the particle-hole continuum boundary, [21] are found at 0.15 and more pronounced at 0.30 eV (B). They imply a very narrow Mott gap of less than 0.3 eV. Narrow Mott gaps from 300 meV to 340 meV were also previously found in Na_{2}IrO_{3} and Li_{2}IrO_{3}. [19] [21] [37] Another discrete transition can be recognized at 0.72 eV (C). It is assigned to t_{2g} intraband transitions from j_{eff} = 3/2 to j_{eff} = 1/2 states. Excitations similar to C were found in other iridates, as well. [21] [26] [38]

A transmission spectrum of the film T was calculated from that of the entire sample T_{sample} and the substrate T_{substrate}, measured each by means of T-FTIR, via T_{sample} × 100/T_{substrate}. [32] The (1-T) spectrum (Fig. 4) also reveal a narrow optical gap below 0.3 eV. Furthermore two broad peaks with shoulders can be discerned indicating electronic excitations. To compare with the IRSE data, the absorption coefficient α, calculated from the MDF, is included in Fig. 4 (blue curve) and the peak positions from Tab. 1 are indicated. Transitions A - C are reproduced in the T-FTIR data but are, however, complemented by transitions B’ and C’ (see Tab. 1).

In summary, we have grown heteroepitaxial Li_{2}IrO_{3} thin films by means of PLD on YSZ(001) substrate. The films exhibit preferential out-of-plane crystalline orientation and defined in-plane epitaxial relationship to the substrate. Resistivity is dominated by three-dimensional variable range hopping. Electronic excitations below 3.34 eV were investigated via spectroscopic ellipsometry and transmission FTIR spectroscopy. On the basis of the j_{eff} physics and by comparison with related iridates, these excitations were associated to d-d transitions, transitions across the Mott gap and in-gap states. The optical gap was found to be ≈ 300 meV, smaller than that of Na_{2}IrO_{3} films.
Table I. Overview of electronic excitations energies in Li$_2$IrO$_3$ thin films determined by IRSE and T-FTIR. The uncertainty is in the order of the last digit.

| Peak | Energy (eV) | $A$ | $B$ | $B'$ | $C$ | $C'$ | $D$ | $E$ |
|------|------------|-----|-----|------|-----|-----|-----|-----|
|      | 0.11, 0.18 | 0.3 | 0.43 | 0.72 | 0.89 | 1.63 | 3.25 |     |
| type of excitation | magnon | $j_{\text{eff}} = 3/2 \rightarrow j_{\text{eff}} = 1/2$ | $j_{\text{eff}} = 3/2 \rightarrow j_{\text{eff}} = 1/2$ | $j_{\text{eff}} = 3/2 \rightarrow j_{\text{eff}} = 1/2$ | $t_{2g} \rightarrow e_g$ | $t_{2g} \rightarrow e_g$ | | |
| | (discrete) | (band-band) | (discrete) | (band-band) | | | | |

Figure 4. (Color online) Optical transmission (1-T) measured by T-FTIR (black) and optical absorption coefficient $\alpha$ (blue) of a Li$_2$IrO$_3$ thin film calculated from the MDF at ambient conditions. Labels $A$ to $C'$ denote relevant excitations related to e.g. $d$-$d$ transitions.

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Please note that such a high surface roughness cannot be exactly described by this approach and the DF of the surface layer with their chosen gradient strongly correlates with the DF of the thin film. Therefore, for absolute values of the thin film DF a uncertainty of $\Delta \varepsilon_2 \approx +20\% / -5\%$ in the worst case has to be taken into account. But nevertheless, their general lineshape and the energy values of the electronic excitations and phonon modes are influenced far less and are therefore reliable. For the same reason we do not report $\varepsilon_1$ because here the error amounts up to 50%.

The reflectivity of the thin film and the substrate is almost constant in that range and small, thus neglecting both introduces an error of less than 5% in $T$. 