Supplemental material to the article

"Magnetic properties of Li_2RuO_3 as studied by the NMR and the LDA+DMFT calculations"

1. Details of crystal growth

To prepare the polycrystalline samples, appropriate quantities of Li_2CO_3 and RuO_2 (both Alfa Aesar, at least 99.99 % purity) were mixed using an agate mortar and pestle and dried in a furnace at 600 °C in air overnight. The powder was then pressed into 10 mm diameter pellets and heated at 900 °C for 15 h followed by sintering in an alumina crucible at 1000 °C for four days, with intermediate grinding. A 10 mol % excess of Li_2CO_3 was used to compensate for evaporation of Li. All heating was done in a muffle furnace. The sample purity was monitored using a Rigaku MiniFlex benchtop X-Ray diffractometer employing Cu-Kα radiation. Our bulk resistivity and differential scanning calorimetry measurements show clear signs of the phase transition at around 560 K, indicative of the high quality of our samples.

2. NMR details

^{7}Li NMR measurements were carried out over the temperature range (100–700) K on the AVANCE III 500WB BRUKER spectrometer in magnetic field $H_0 = 11.74$ T. The static broad spectra of ^{7}Li (the nuclear spin $^7I = 3/2$; quadrupole moment $^7Q = -0.04 \times 10^{-24}$ cm^2) were obtained by means of the spin echo signals with subsequent Fourier transformation of the acquired signals. The magic angle spinning (MAS) NMR spectra of ^{7}Li were obtained using a 3.2 mm rotor with a spinning speed of about 20 kHz. The ^{7}Li NMR signal in LiCl solution was used as a frequency reference $\nu_0 = (\gamma/2\pi)H$ for the shift of NMR lines. The parameters of the electric field gradient (EFG) tensor, V_{ii}, quadrupole frequency, $\nu_Q = (3eQ/2I(2I-1)h)V_{ZZ}$, and asymmetry parameter, $\eta = (V_{XX} - V_{YY})/V_{ZZ}$ – were determined by computer simulation of the MAS NMR ^{7}Li spectra [15].

3. Calculation details

We used the local density approximation (LDA) and the tight-binding linear muffin-tin orbital (TB-LMTO) method [25] to generate the noninteracting band structure, which was used in the LDA+DMFT (cluster) calculations. The crystal structure was taken from Ref. 6. The calculations were performed on a dense mesh of 1728 k-points in a full Brillouin zone. The Wannier function projection method [24] was employed to construct the low energy Hamiltonian for the Ru-t_{2g} states.

As it was shown earlier, in the DFT calculations Li_2RuO_3 is metallic in both low and high temperature phases [8], which contradicts to the experimental observation [6]. If we adopt Hubbard U correction in simplified methods such as LDA+U, we will stabilize solutions with electrons localized on the sites, not on the bonds and hence spoil molecular orbitals, which are obviously responsible for the formation of the spin-gap in Li_2RuO_3. Single site dynamical mean-field theory (DMFT) is also useless in this situation. Only the cluster extension of the LDA+DMFT calculation is able to treat the tendency to form the molecular orbital state and the strong Coulomb correlations (inherent to transition metals with unoccupied d shell) on equal footing.

The effective impurity model was solved by the Hirsh-Fye algorithm (HF-QMC) [23]. We chose typical values of the Hubbard repulsion parameter and Hund's exchange for Ru^{4+}: $U = 3$ eV and $J_H = 0.7$ eV [26, 27]. The LDA+DMFT calculations were performed using the AMULET code. The uniform magnetic susceptibility was calculated as response to an external magnetic field.

$$\chi = \left.\frac{\delta m}{\delta h}\right|_{h\to 0} = \frac{n_\uparrow - n_\downarrow}{\delta E}\mu_B^2, \tag{1}$$

where δh is a small applied magnetic field, δE is corresponding Zeeman splitting (20 meV), $\delta m(T)$ is a magnetization, $n_\uparrow$ and $n_\downarrow$ are the total occupation numbers for spin up and down.

We used nonmagnetic generalized gradient approximation [15] and linearized augmented plane wave method as realized in Wien2k package [16] to calculate electric field gradient tensor.