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Dimerization in honeycomb Na$_2$RuO$_3$ under pressure: a DFT study

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Compounds with the honeycomb lattice are under intensive study in last two decades, since many of them show intriguing and sometimes rather unexpected physical properties [1–15]. One of the examples is Li$_2$RuO$_3$. This is a layered material. In the low-temperature (LT) phase two out of six Ru–Ru bonds in a hexagon dimerize, which results in formation of the spin gap [16]. With increase of temperature Li$_2$RuO$_3$ exhibits an unusual phase transition at $T_d \sim 540$ K, which was initially thought as a transition from a dimerized to uniform structure [17]. However, more careful study using X-ray pair distribution function analysis shows that dimers as rigid units survive even at $T > T_d$, while in the average this system can be described as undimerized, uniform (C2/m space group) [18, 19]. Surprisingly, similar compound Na$_2$RuO$_3$ order magnetically below $T_N \sim 30$ K (AFM zigzag) without any sizeable structural distortions in honeycomb lattice [20, 21]. In high-temperature phase Na$_2$RuO$_3$ crystallizes in the same C2/m space group as Li$_2$RuO$_3$, but the volume of the unit cell in Na$_2$RuO$_3$ is $\sim 5\%$ larger. Thus, one might expect that under the pressure Na$_2$RuO$_3$ may start to dimerize and will exhibit all unusual properties as its sister compound Li$_2$RuO$_3$.

In the present work we study a possible formation of the dimerized crystal structure in Na$_2$RuO$_3$ under pressure using Vienna Ab-initio Simulation Package (VASP) [22, 23] in the generalized gradient approximation (GGA). Analysis of the electronic structure was performed within the TB-LMTO-ASA code, which is based on the linearized muffin-tin orbital method [24]. In order to create dimerized Na$_2$RuO$_3$ structure the LT Li$_2$RuO$_3$ structure with $P2_1/m$ space group was choosen.

The volume dependence of total energies, E, is presented in Fig. 1a. The uniform structure of Na$_2$RuO$_3$, which is experimentally observed at ambient pressure, does have the lowest total energy and this structure corresponds to the global minimum of $E(V)$ in the GGA.
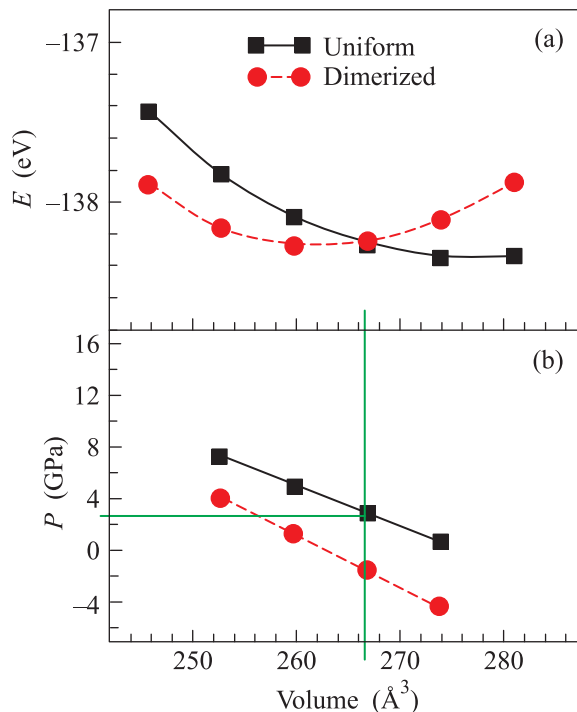

Fig. 1. (Color online) (a) – Total energy dependence of Na$_2$RuO$_3$ of two structures (with and without structural Ru-Ru dimers) for different volumes. (b) – Pressure dependence on the volume for these two structures

However, the situation changes with decrease of the volume and the dimerized structure turns out to be the lowest in energy for $V < 266$ Å^3.

In order to estimate the critical pressure in Na$_2$RuO$_3$ we first interpolated $E(V)$ (to have a smooth function) and then recalculated the pressure dependence on volume as $P = -\partial E/\partial V$, which is shown in Fig. 1b. Applying external pressure to undimerized phase of Na$_2$RuO$_3$ we reduce volume of the unit cell down to critical value V_{undim}, when the total energies of uniform and dimerized phases are the same. This point defines a critical pressure for transition, $P_c \sim 3$ GPa, see Fig. 1b. Further compression drives the system to the dimerized phase. Corresponding jump in the unit cell volume at the tran-

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sition is $\delta V = V_{\mathrm{undim}} - V_{\mathrm{dim}} \sim 10\,\text{Å}^3$. Similar transition in Li_2RuO_3 (but caused by temperature) gives $\delta V \sim 8\,\text{Å}^3$ [16].

Thus we found that one may expect a structural transition in Na_2RuO_3 at $\sim 3\,\text{GPa}$. One may expect that this transition will be accompanied by strong changes in the magnetic and electronic properties, related to the formation of the spin gap and strong bonding-antibonding splitting.

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