Combined High Pressure and Low Temperature Structural Studies of $SrRuO_3$

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Perovskites with 4*d* and 5*d* transition metals have received growing attention because of their interesting physical properties, which are highly sensitive to variations in the structure [1]. $SrRuO_3$ stands out against other 4*d* transition metal oxides due to its surprising itinerant ferromagnetism; it is the only ferromagnetic ABO_3 perovskite compound displaying a relatively high Curie temperature of 163 K [2]. Because of the observed unique properties of $SrRuO_3$, it is widely used as a metallic perovskite electrode in oxide based spintronic and electronic devices [3]. $SrRuO_3$ has also been proposed as a candidate compound to display exotic quantum critical phenomena, such as unconventional superconductivity and non-Fermi-liquid behavior [4,5], which can be triggered by application of external hydrostatic pressure, magnetic fields or chemical doping [6,7].

$SrRuO_3$ adopts the perovskite structure (orthorhombic space group P*nma*) at ambient pressure. Two independent studies predicted a ferromagnetic perovskite to non-magnetic post-perovskite transition in $SrRuO_3$ at 32 GPa [8] and 40 GPa [9], respectively, using first-principles calculations based on density functional theory (DFT). These are so far in conflict with experimental observations, as the post-perovskite have not been observed experimentally for $SrRuO_3$ to this day. The discovery of a structural phase transition to the post-perovskite in the $MgSiO_3$ at 125 GPa sparked a great interest in discovering analogue materials with the perovskite to post-perovskite transition. The post-perovskite phase of $MgSiO_3$ is a major component in the lower mantle of the Earth and knowledge of its physical properties is of great importance for understanding the dynamics of the mantle. As $MgSiO_3$ post-perovskite is only stable at extreme pressures, it is important to combine theoretical calculations with experiments on analogue post-perovskite ABO_3 compounds, which are stable at ambient pressure and temperature, and the scientific community is still searching for such materials.

High pressure studies of $SrRuO_3$ have previously been reported up to 53 GPa at low temperature (6 K) [10], where they observed a second order transition to the lower symmetry space group monoclinic $P2_1/n$ in the range from 10 to 21 GPa. At 38 GPa they observed a first order transition to a triclinic structure accompanied by a volume collapse of 3.5%. A similar study have been reported up to 34 GPa [11], where they observed a minimum in the Ru-O-Ru angle at 15 GPa, but no phase transitions were observed. In this study they also investigated the pressure dependence of the Curie temperature, which was reported to drop to 42.7 K at 17.2 GPa with an almost linear rate of dT_c/dP = -6.8 K/GPa. We have performed new high pressure studies of $SrRuO_3$ to 88 GPa at ambient temperature and to 65 GPa at 6 K. We observe the second order transition to the monoclinic space group ($P2_1/n$) at around 25 GPa for both the ambient temperature and 6 K experiment, which is consistent with the transition observed at previous reported data collected at 6 K [10]. However, we did not observe any second order transition with an accompanied volume collapse in either of the experiments as shown in figure 1, where the volume data obtained from our two experiments are compared. The bulk modulus (K_0) was determined using the 3th order Birch-Murnaghan (BM3) equation of state (EoS) and the fits are shown in Figure 1. Using this we obtain a bulk modulus of K_0 = 168(14) GPa for the data measured at ambient temperature and a bulk modulus of K_0 = 161(7) GPa for the data measured at 6 K.

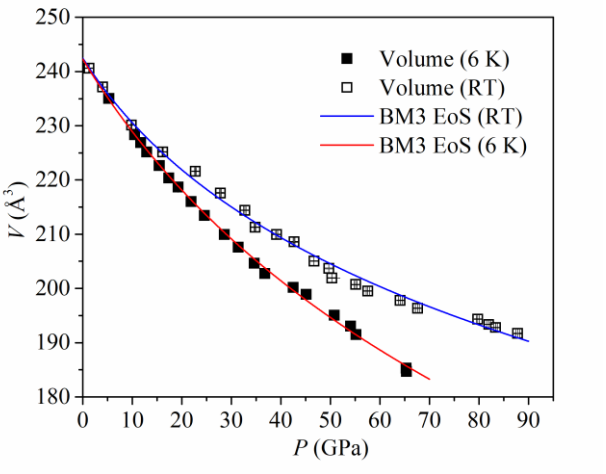

Figure 1. *P-V* relation for $SrRuO_3$ fitted with the BM3 EoS.

There is conflict in the reported literature concerning the relationship between the unit cell parameters as a function of pressure and contradictory phase transitions have been observed in different experiments [10-12]. Some studies show crossovers between the cell parameters, while others do not. The contradictory observations suggest that the magnetic ordering of the structure induced by low

temperature could be important for the pressure induced phase transitions and unit cell relationship in $SrRuO_3$. We therefore investigated the effect of low temperature magnetic ordering in $SrRuO_3$ by conducting an experiment at a fixed pressure of 40 GPa, just above the 38 GPa where the first order phase transition to the triclinic phase was previously observed at 6 K [10]. At the 40 GPa we cooled the sample slowly from 300 K to 6K, to investigate if we could induce the same phase transition and at what temperature it would happen. In connection with the experiments, we have also performed magnetic and non-magnetic DFT calculations and see that the magnetic moment persists to above 75 GPa. The calculated magnetic moment is ~2 μ_B per Ru ion at ambient pressure and decreases as a function of pressure. However, the rate of decrease of the magnetic moment is not constant, and almost plateaus between 40 and 60 GPa. Then, the magnetic moment vanishes at higher pressure, larger than 75 GPa. The low temperature did not induce the phase transition and we do not observe a first order phase transition in any of our experiments.

The results from these experiments combined with the thorough theoretical investigation have given much more insight on the compressibility of the orthorhombic perovskite $SrRuO_3$ and the role temperature plays during compression clarifying contradictions in the literature.

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