Pressure Effects on Orbital Ordered States in Perovskite-Type Vanadium Oxides

The effects of pressure on orbital ordered states in perovskite-type vanadium oxides, RVO_3 (R=Y, Tb), have been systematically investigated using a high-pressure, low-temperature X-ray diffraction technique. The universal pressure-temperature phase diagram of the orbital state in RVO_3 was clearly determined. The phase diagram reveals a general stabilization of the C-type orbital ordering (C-OO) phase with applied hydrostatic pressure. We propose that covalency effects among the R-ion d, the oxygen $2p$, and the vanadium $3d$ orbitals plays an important role in the C-OO stabilization.

Various intriguing physical properties have been discovered in transition metal oxides, such as high T_C superconductivity, colossal magnetoresistance effects, and magnetoelectric effects. The strong coupling between the charge, the spin and orbital the 3d electrons, and the lattice degrees of freedom play important roles in these effects. Hence the study of these electronic states is important for understanding the phenomena microscopically.

Perovskite-type vanadium oxides, RVO_3 (R: rare earth), have two 3d electrons on the V^{3+} ions, which have the orbital degree of freedom of t_{2g} electron. As a result, RVO_3 shows various physical properties due to the coupling of the orbital and spin states. The orbital state can be directly controlled by the application of pressure, since it is strongly coupled with the lattice distortion, i.e. the Jahn-Teller distortion. Here we study pressure effects on the orbital ordered states of perovskite-type vanadium oxides. Two types of orbital ordering, C-type orbital ordering (C-OO) and G-type orbital ordering (G-OO), have been reported as the ground state in the RVO_3 system, and the orbital ground state varies as a function of the R-site ionic radius [1]. YVO_3 and $TbVO_3$ have C-OO and G-OO phases as the ground states, respectively, and are located near the phase boundary between these orbital states. Hence we expected the orbital states to respond sensitively to the application of hydrostatic pressure. The pressure-temperature phase diagram for the orbital state was investigated in YVO_3 and $TbVO_3$ for applied pressures of up to 10 GPa [2].

High-quality single crystals of RVO_3 (R = Y, Tb) were grown using a floating-zone method. For the high-pressure and low-temperature experiments, a helium gas-pressure driven diamond anvil cell (DAC) was mounted on a closed-cycle helium refrigerator. The sample pressure was controlled by varying the helium gas pressure. The sample pressure was calibrated from the lattice constant of a crystal of NaCl enclosed with the sample in the DAC. The single crystal X-ray diffraction experiment was performed using BL-4C and 9C.

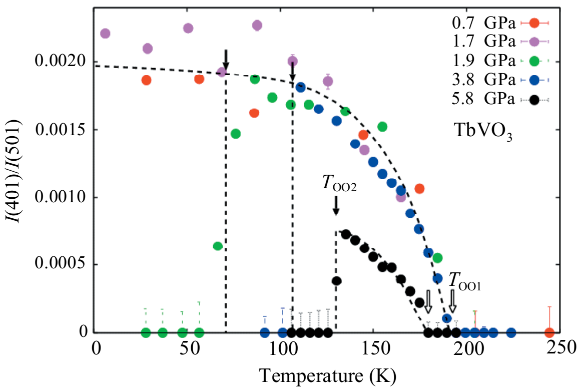

Figure 1
Temperature dependence of the (4 0 1) reflection intensity for $TbVO_3$ for applied pressures of up to 5.8 GPa. The intensity of the (4 0 1) reflection is normalized by that of the (5 0 1) fundamental reflection. The open and closed arrows indicate T_{OO1} and T_{OO2}, respectively.

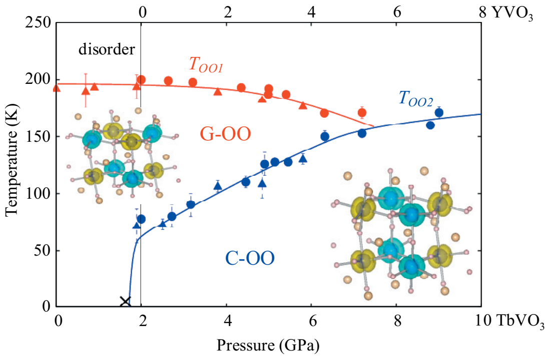

Figure 2
Pressure-temperature phase diagram of the orbital state for YVO_3 and $TbVO_3$. Circles and triangles represent the transition temperatures of YVO_3 and $TbVO_3$, respectively. The pressure scale for YVO_3 has been shifted by 2 GPa relative to that of $TbVO_3$.

The orbital disordered (OD) and C-OO phases have an orthorhombic lattice with the space-group *Pbnm*, while the G-OO phase has a monoclinic lattice with $P2_1/b$. Therefore the change from the orthorhombic to the monoclinic lattice can be evaluated by the (4 0 1) reflection, which is a forbidden reflection in *Pbnm* but a fundamental one in $P2_1$/b. We therefore determined the orbital phase diagram using this reflection. The temperature-pressure dependence of the (4 0 1) reflection was measured in $TbVO_3$ as shown in Fig. 1. In the pressure experiment below 1.7 GPa, the intensity of the (4 0 1) reflection appears below T_{OO1} and survives even at the lowest temperature. Hence the G-OO phase appears below T_{OO1} as the ground state. Above 1.9 GPa, on the other hand, the (4 0 1) intensity suddenly disappears below T_{OO2}. This suggests that the crystal symmetry becomes higher than that of $P2_1/b$, and the structural phase transition can be assigned to the G-OO/C-OO one at T_{OO2}. The pressure-temperature phase diagram of $TbVO_3$ and YVO_3 was determined on the basis of these experiments (Fig. 2). The phase diagram strongly suggests a general stabilization of the C-type orbital ordering (C-OO) phase under the application of hydrostatic pressure. The pressure dependence of T_{OO1} and T_{OO2} in $TbVO_3$ is quite similar to that in YVO_3. The phase diagram of $TbVO_3$ could be well scaled to that of YVO_3 with a shif of 2 GPa; namely the effect of the Y substitution for Tb corresponds to that of a hydrostatic pressure of 2 GPa. Finally, we have elucidated the universal pressure-temperature phase diagram for the orbital states in the RVO_3 system.

Here we discuss the mechanism stabilizing the C-OO phase under hydrostatic pressure. In the R-ion substitution studies, the ground state changes from the C-OO to the G-OO phase with increasing R-ion radius. The one-electron bandwidth W was previously considered to be a key parameter, since W increases with increasing R-ion radius. However, the pressure effect on the orbital ordering cannot be explained by the pressure dependence of the band width. We thus considered the covalency effect to understand the pressure effect for the orbital state. Because the ions approach each other, owing to the contraction of the unit-cell volume under high pressure, the hybridization between orbitals increases. According to the crystal structure studies for YVO_3 at ambient pressure, the distance between the Y and V ions in the C-OO phase is smaller than that in the G-OO phase [3]. As a result, a covalent character between the V-3d and R-d orbitals is developed in the C-OO phase; the energy gain due this covalency is larger than that in the G-OO phase. Hence it is likely that the C-OO phase is stabilized when the covalency effect increases under high pressure. This is a new view point for the stabilization of orbital ordering.

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4C and 9C

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