Hollandite: a novel class of oxides with unusual properties

Prof. Dr. Yutaka Ueda
Institute for Solid State Physics
University of Tokyo

Hollandites: $K_xM_8O_{16}$ (M = Ti, V, Cr, and Mn) give us a chance to systematically study electron correlation effect as a function of electron filling. The common structure is made of double-chains (zigzag-chains) formed by edge-sharing MO_6 octahedra. Such double-chains are interconnected through common corners to form M_8O_{16}-framework with tunnels. The sites within the tunnels are occupied by K ions which donate electrons to the M_8O_{16}-framework, leading to a mixed valence of $M^{3+}/M^{4+} = 1/3$ at $x = 2$. $K_2Ti_8O_{16}$ with a relatively lower electron filling is a Pauli paramagnetic metal [1]. $K_2V_8O_{16}$ [2,3] and $K_2Cr_8O_{16}$ [4] with higher electron fillings show metal-insulator (MI) transitions. $K_2V_8O_{16}$ exhibits a first order MI transition at 170 K, accompanied by charge order between V^{4+} and V^{3+} and the formation of V^{4+}-V^{4+} spin-singlet pairs and V^{3+}-V^{3+} pairs in the low temperature insulator phase. On the other hand, $K_2Cr_8O_{16}$ is a ferromagnetic metal with $T_C = 180$ K, which is explained by the double exchange mechanism, but surprisingly this ferromagnetic metal phase undergoes a transition to an insulator at $T_{MI} = 95$ K, remaining ferromagnetic. Recent structural study by synchrotron x-ray diffraction of the single crystal and electronic structure calculation have revealed that this novel ferromagnetic MI transition is caused by the Peierls instability in the quasi-one-dimensional column structure made of four coupled Cr-O chains, leading to the formation of tetramer of Cr ions [5]. The manganese hollandite has K-deficiency as $K_{1.6}Mn_8O_{16}$. $K_{1.6}Mn_8O_{16}$ shows a structural transition at 250 K, accompanied by K-vacancy order and simultaneous charge order between Mn^{3+} and Mn^{4+}. $K_{1.6}Mn_8O_{16}$ has one extra e_g-electron per five Mn^{4+} ions and these extra electrons could be trapped by Mn ions adjacent to K-vacancies, resulting in Mn^{3+} state or a polaronic state of $Mn^{+4-\delta}$ and $Mn^{+3+\delta}$. Such an electron trapping at Mn ions near K-vacancies would be realized even in the disordered state of K-vacancies and would be responsible for the observed variable range hopping type conductivity in the wide temperature region.

References

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