Theory on electronic structure and phase transitions in V_2O_3

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Abstract

The electronic structure and phase transitions in pure and Cr doped V_2O_3 are studied in relation to the 3*d* spin-orbit interaction and the monoclinic lattice distortion. A finite-size cluster model consisting of V ions is studied within the many-body point of view. No orbital ordering is expected to be present in the antiferromagnetic insulating (AFI) phase and instead of this a large orbital magnetic moment $\sim 0.7\mu_B$ exists. In the AFI and paramagnetic insulating (PI) phases, Jahn-Teller like lattice instability causes tilting of the nearest-neighbor V ion pairs from the corundum *c*-axis and this lead to large difference in the 3*d* orbital occupation between the metallic and insulating phases. To investigate the AFI to PI transition in Cr doped system, a model spin-lattice Hamiltonian is also proposed. The transition is found to be a simultaneous order-disorder transition of the magnetic moments and the tilting of the V ion pairs.

Key words: V2O3; spin-orbit interaction; lattice distortion; orbital ordering

Although V_2O_3 is often referred to a typical example of the Mott-Hubbard system, there are experimental facts showing importance of electron-lattice interaction and 3*d* orbital degeneracy, which can not be explained within the single-band Hubbard model. Recent measurements on the linear dichroism of V 2*p* x-ray absorption spectra (XAS) [2] and resonant x-ray scattering experiments (RXS) [1] bring new information about its electronic structure, stimulating discussions on this compound. Based on the information, the author has developed a novel theory on the 3*d* electronic state and the phase transitions in V_2O_3 and its Cr doped alloys [3].

To discuss the 3*d* electronic state of V_2O_3, a V ion cluster model consisting of the nearest-neighbor V ions pair along the corundum *c*-axis was considered on the basis of the configuration interaction approach. In the model, the 3*d*-3*d* multipole interaction, a trigonal crystal field and the 3*d* spin-orbit interaction were considered and electron hopping between the nearest neighbor V ions was also taken into account. In V_2O_3, the O_h crystal field splits the 3*d* orbitals of each V ion into two fold e_g and three fold t_{2g} orbitals and the t_{2g} orbitals are further separated into low laying two fold e^π and non-degenerate a_1 orbitals by small trigonal field. Because of the hybridization of the 3*d* orbitals between the two V ions, the electron configuration of each V ion is not $e^\pi e^\pi$ as is expected from the ionic limit. The configurations between the two V ion sites strongly correlate and the electronic stat of the V ion pair is described as a superposition of the two configurations $e^\pi a_1; e^\pi e^\pi$ (the $e^\pi a_1$ configuration on one of the V ion and the $e^\pi e^\pi$ on the other) and $e^\pi e^\pi; e^\pi a_1$ in equal weight with $S = 1$ spin state in both V ions.

Although the results above are the same to those obtained in the model proposed by Mila *et al.* [4,5], fundamental difference between two models arises from the 3*d* spin-orbit interaction, which is not included in their model. In the presence of the 3*d* spin-orbit interaction, the spin and orbital degree of freedoms are strongly coupled and this removes the two fold orbital degeneracy of the $e^\pi a_1; e^\pi e^\pi$ ($e^\pi e^\pi; e^\pi a_1$) ground state and the ground state has a large orbital magnetic moment $\sim 0.7\mu_B$. The large orbital moment is in accordance

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with the ratio $M_{\rm L}/M_{\rm S} \sim -0.3$ deduced from the magnetic x-ray scattering experiment [1] and also explains the small total magnetic moment $1.2\mu_{\rm B}$ observed in the AFI phase [6].

Because of the presence of the large orbital magnetic moment, the monoclinic lattice distortion in the AFI phase and the direction of the magnetic easy axis is connected. Since the V-V bond direction of the V ion pair is tilted from the corundum c-axis in the AFI phase and this breaks the three fold rotational symmetry of the c-axis, the state having the $e^{\pi}e^{\pi}$ configuration on both V ion sites (denoted by $e^{\pi}e^{\pi};e^{\pi}e^{\pi}$) is further hybridized with above mentioned $e^{\pi}a_1;e^{\pi}e^{\pi}$ $(e^{\pi}e^{\pi};e^{\pi}a_1)$ state in the ground state. As a result, the easy axis of the magnetic moment is canted from the corundum c-axis in the presence of the monoclinic distortion and this agrees with the neutron diffraction experiments [6].

From the consideration of the lattice distortion energy, it is expected that there is at least two local minima for the free energy in the real system as a function of the V-V distance of the pair. One is positioned at the V-V distance in the PM phase, where the energy difference of the two kinds of the states $e^{\pi}a_1;e^{\pi}e^{\pi}$ and $e^{\pi}e^{\pi};e^{\pi}e^{\pi}$ is large and thus no electron-lattice coupling takes place. The other one is located at the V-V distance in the PI and AFI phases, where energies of the two kinds of the states are nearly degenerate and Jahn-Teller like lattice distortion is the cause of the energy lowering at this V-V distance. Because of the tilting of the V ion pair caused by this lattice instability, the $e^{\pi}e^{\pi};e^{\pi}e^{\pi}$ state is further hybridized with the $e^{\pi}a_1;e^{\pi}e^{\pi}$ $(e^{\pi}e^{\pi};e^{\pi}a_1)$ in these insulating phases. Note that this lattice instability does not originate from the orbital degeneracy of the $e^{\pi}a_1;e^{\pi}e^{\pi}$ $(e^{\pi}e^{\pi};e^{\pi}a_1)$ state as is expected in Mila's model. This large difference in the electron occupation between the metal and insulating phases agrees with the recent linear dichroic V $2p$ XAS experimental results [2].

Since both in the AFI and PI phases, the electron-lattice coupling strongly influences the orbital occupation and charge fluctuation, the PM $\rightarrow$ AFI and PM $\rightarrow$ PI transitions can not be regarded as usual Mott transition. The elongation of the V-V distance and resultant reduction in the hybridization strength between the $3d$ orbitals caused by this electron-lattice coupling is probably responsible for these metal-insulator transitions.

To investigate interplay between magnetic ordering and the lattice distortion, an effective spin Hamiltonian including the effects of tilting of the V ion pairs was introduced. The antiferromagnetic order with the monoclinic lattice distortion observed in the AFI phase was reproduced in this model, where simultaneous ordering of the tilting directions and the magnetic moments of the V ion pairs take place. With increasing temperature, it exhibits antiferromagnetic to paramagnetic phase transition corresponding to the AFI $\rightarrow$ PI transition in Cr doped V_2O_3. While all V ion pairs are tilted to the same direction and this gives rise the monoclinic lattice distortion in the AFI phase, their tilting directions are disordered and fluctuate among the three stable directions in the PI phase. As a result, there is no monoclinic distortion in the PI phase. It was also found that the C_{44} elastic constant softens and short-range spin correlation functions abruptly changes at this second order transition in this model. These results are consistent with the ultrasonic-wave measurement [8] and recent neutron scattering experiments [7].

The experiments on RXS at the V K-edge [1] and the linear dichroic V $2p$ XAS experiments [2] were analyzed, using above model. The (111) Bragg reflection observed in the RXS experiments, particularly in its azimuthal angle and polarization dependence of the $1s \rightarrow 3d$ peak, is well explained within the present model, where no orbital ordering is present and the antiferromagnetic order is assumed. The reflection is pure magnetic and the scattering amplitude of this reflection mainly arises from the interference process of the $1s \rightarrow 4p$ dipole and $1s \rightarrow 3d$ quadrupole transitions. The shape and magnitude of the linear dichroic V $2p$ XAS spectra in both the AFI and PM phases are well reproduced within the present model.

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