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A new half-metallic ferromagnet $K_2Cr_8O_{16}$ predicted by an *ab-initio* electronic structure calculation

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Abstract. The first-principles electronic structure calculation is carried out to predict that a chromium oxide $K_2Cr_8O_{16}$ with the hollandite-type crystal structure should be a new half-metallic ferromagnet. We compare our results with recent experimental data which indicate the ferromagnetic-metal to ferromagnetic-insulator transition at $T \sim 90$ K, as well as the paramagnetic-metal to ferromagnetic-metal transition at $T \sim 180$ K. Based on the calculated electronic structures, we argue that the double-exchange mechanism is responsible for the observed saturated ferromagnetism and the formation of the incommensurate, long-wavelength density wave of spinless fermions caused by the Fermi-surface nesting may be the origin of the opening of the charge gap.

1. Introduction

Recently, it has been reported [1] that a chromium oxide $K_2Cr_8O_{16}$ of hollandite type shows a phase transition from the paramagnetic metal to ferromagnetic metal at $T_c \simeq 180$ K by lowering temperatures, where the ferromagnetic state has a full spin polarization of 18 μ_B per formula unit (f.u.) at low temperatures. In addition to this phase transition, it has also been reported [1] that another phase transition occurs from the ferromagnetic metal to ferromagnetic insulator at $T_{MI} \simeq 90$ K, suggesting that the charge gap opens below T_{MI}. However, no structural distortions associated with this metal-insulator transition (MIT) have been observed so far [1]. The mechanism of MIT of this material has therefore been a great puzzle.

The crystal structure of $K_2Cr_8O_{16}$ (see Fig. 1) belongs to a group of hollandite-type phases where one-dimensional (1D) double strings of edge-shared CrO_6 octahedra forms a Cr_8O_{16} framework of a tunnel structure, wherein K ions reside [2]. Cr ions are in the mixed-valent state of Cr^{4+} (d^2) : Cr^{3+} (d^3) = 3 : 1, and hence with 2.25 electrons per Cr ion.

In this paper, we perform the first-principles electronic structure calculations based on the generalized gradient approximation (GGA) in the density-functional theory in order to clarify the origins of ferromagnetism and MIT of $K_2Cr_8O_{16}$. We thereby predict that the materials $A_2Cr_8O_{16}$ (A = K and Rb) belong to a new class of half-metallic ferromagnets [3]; i.e., the majority-spin electrons are metallic, whereas the minority-spin electrons are semiconducting with a band gap. We also show from the GGA and GGA+U [4] calculations that the double-exchange mechanism is responsible for the observed saturated ferromagnetism. We then discuss possible mechanisms of the MIT and argue that the formation of an incommensurate, long-
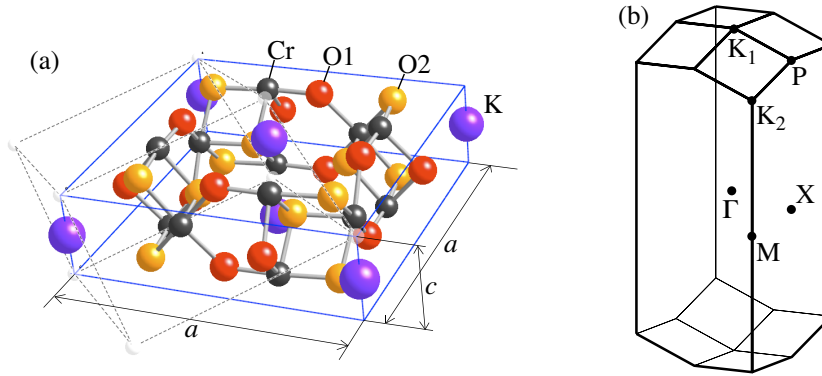
Figure 1. Schematic representations of (a) the unit cell of the body-centered tetragonal lattice (solid lines) and (b) Brillouin zone of $K_2Cr_8O_{16}$. In (a), the primitive unit cell is also shown in the thin dotted lines. In (b), the symbols represent $\Gamma(0,0,0)$, $M(2\pi/a, 0, 0)$, $X(\pi/a, \pi/a, 0)$, $P(\pi/a, \pi/a, \pi/c)$, $K_1(0, 0, \pi(1/c + c/a^2))$, and $K_2(2\pi/a, 0, \pi(1/c - c/a^2))$, where K_1 and K_2 are equivalent.

wavelength spin and charge density wave (DW) due to Fermi-surface nesting may be the origin of MIT of this material.

2. Method of calculation

For the GGA calculations, we employ the computer code WIEN2k [5] based on the full-potential linearized augmented-plane-wave method. The spin polarization is allowed. The spin-orbit interaction is not taken into account. The GGA+U calculation [4] is also made to see the effects of on-site electron correlation U on the band structure. We assume the experimental crystal structure of $K_2Cr_8O_{16}$ observed at room temperature with the lattice constants of $a = 9.7627$ and $c = 2.9347$ Å[2]. The Bravais lattice is body-centered tetragonal and the primitive unit cell (u.c.) contains four crystallographically equivalent Cr ions, one K ion and eight O ions, i.e., KCr_4O_8, as shown in Fig. 1.

3. Results of calculation

We first find that the ground state in GGA is fully spin-polarized with the magnetic moment of 9.000 μ_B/u.c. in consistent with experiment [1]; the energy gain of 3.16 eV/u.c. is obtained by the spin polarization. The calculated density of states (DOS) is shown in Fig. 2 in a wide energy range covering over the O 2p and Cr 3d bands. We find three separate peaks in both the majority and minority spin bands, which are the O 2p peak, Cr 3d peak with the t_{2g} symmetry, and Cr 3d peak with the e_g symmetry. The hybridization between the O 2p and Cr 3d bands is significantly large. The Fermi level is located at a deep valley of the t_{2g} majority-spin band while it is located in the energy gap between the O 2p and Cr 3d t_{2g} bands of the minority-spin band. Thus, the half metallicity of this material is evident in the calculated DOS.

We also calculate the orbital-decomposed partial DOS, $\rho_\alpha(\varepsilon)$ ($\alpha = xy, yz, zx$), in the Cr 3d t_{2g} region, where the two components are exactly degenerate, $\rho_{yz}(\varepsilon) = \rho_{zx}(\varepsilon)$. The three t_{2g} orbitals are almost equally occupied by electrons in the paramagnetic state. In the ferromagnetic state, however, the d_{xy} orbitals is almost fully occupied by electrons and therefore holes are only in the d_{yz} and d_{zx} orbitals. Also, the d_{xy} component has a rather high peak-like structure at $\sim$0.7 eV below the Fermi level, indicating an essentially localized character of the d_{xy} electrons. The d_{yz} and d_{zx} components, on the other hand, have a rather wide band spreading over $\sim$1 eV around the Fermi level, indicating an itinerant character of the d_{yz} and d_{zx} electrons. The situation may
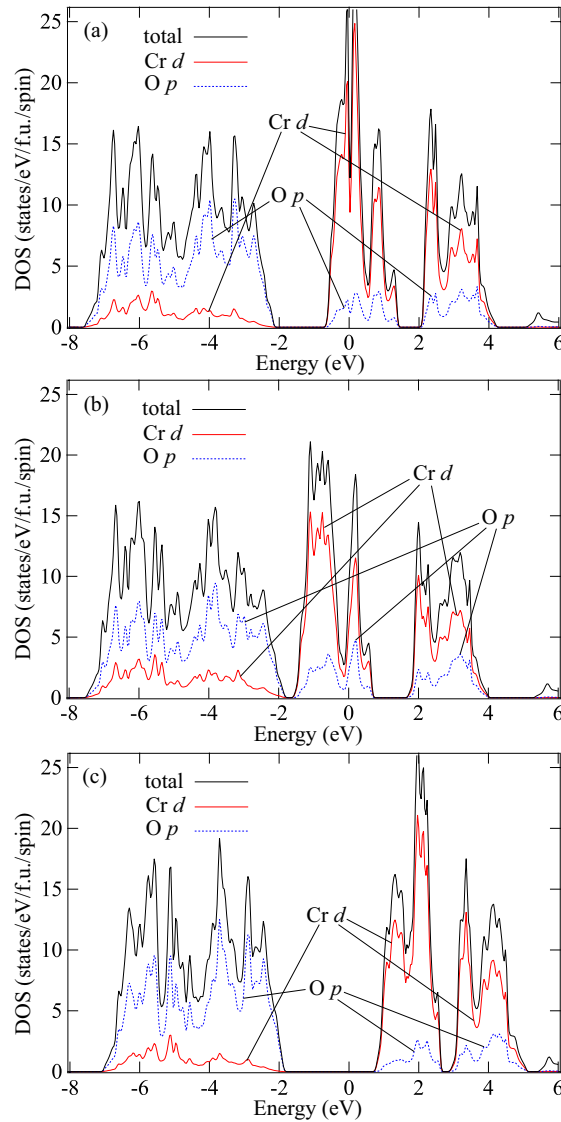
Figure 2. Calculated result for the DOS (per spin per formula unit (f.u.)) of $K_2Cr_8O_{16}$ in a wide energy range for (a) the paramagnetic state, and (b) majority-spin and (c) minority-spin bands in the ferromagnetic state. The Fermi level is set to be the origin of energy.

be clarified further if we observe the calculated band dispersion near the Fermi level. We find that a rather dispersionless narrow band of predominantly d_{xy} character is located at ~ 0.7 eV below the Fermi level, extending over a large region of the Brillouin zone. On the other hand, the dispersive t_{2g} bands of predominantly d_{yz} and d_{zx} character with strong admixture of the $2p_z$ state of O(2) are located around the Fermi level.

We thus have the dualistic situation where the essentially localized d_{xy} electrons at ~ 0.7 eV below the Fermi level interact with the itinerant d_{yz} and d_{zx} electrons of the bandwidth comparable with the intraatomic exchange energy of ~ 1 eV, whereby the Hund's rule coupling gives rise to the ferromagnetic spin polarization via the double-exchange mechanism [6]. To support this further, we make the GGA+U calculation for the present material. We find that, as U increases, the d_{xy} band shifts further away from the Fermi level, leaving essentially no

weight above the Fermi level, whereas the d_{yz} and d_{zx} bands with strong admixture of the O(2) $2p_z$ states are much less affected by the presence of U. These results are consistent with what is expected in the double-exchange mechanism of ferromagnetism.

We also calculate the Fermi surface of $K_2Cr_8O_{16}$ in the ferromagnetic state. There are 12 t_{2g} bands, 3 of which cross the Fermi level and form the semimetallic Fermi surfaces; i.e., the second and third bands (counted from the top) form the electron Fermi surfaces and the fourth band forms the hole Fermi surface. The wave functions at the Fermi surfaces have predominantly d_{yz} and d_{zx} character with large admixture of the O(2) $2p_z$ states. We also find that there is a pair of the 1D-like parallel Fermi surfaces, which are seen to have a very good nesting feature. The nesting vector is aligned roughly along the Γ-K_1 direction and has the value $\mathbf{q}^* \simeq (0, 0, 0.147)2\pi/c$ or $(0, 0, 0.853)2\pi/c$. Thus, the Fermi-surface instability corresponding to the wavenumber $\mathbf{q}^*$, leading to formation of the incommensurate, long-wavelength (with a period of $\sim$7c in the real space) DW, may be relevant with the opening of the charge gap in the present material. Note that the spin and charge DWs occur simultaneously with the same wavenumber $\mathbf{q}^*$ since we have only the up-spin electrons.

To confirm the nesting features more precisely, we calculate the generalized susceptibility $\chi_0(\mathbf{q})$ for the noninteracting band structure, where we find that the sharp peak structure at $q_z^* = 0.295\pi/c$ and $1.705\pi/c$ remains strong, irrespective of the value of (q_x, q_y), although there is a small variation in the (q_x, q_y) plane. The true maximum appears at $\mathbf{q}^* \simeq (\pi/a, \pi/a, q_z^*)$, or around $(\pi/a, \pi/a, q_z^*)$ slightly deviating and splitting from $(\pi/a, \pi/a, q_z^*)$ in the (q_x, q_y) plane. Thus, if we include the effects of electron correlations, the $\mathbf{q}$-dependent susceptibility can diverge at this momentum $\mathbf{q}^*$, resulting in the formation of the incommensurate, long-wavelength charge and spin DW, which we hope will be checked by experiment in near future.

Details of our calculations will be published elsewhere [7].

4. Summary
We have made the first-principles electronic structure calculations and predicted that a chromium oxide $K_2Cr_8O_{16}$ of hollandite type should be a half-metallic ferromagnet. We have shown that the double-exchange mechanism is responsible for the observed saturated ferromagnetism. We have argued that the formation of the incommensurate, long-wavelength density wave of spinless fermions caused by the Fermi-surface nesting may be the origin of the opening of the charge gap. We hope that these predictions will be checked by further experimental studies.

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