

Charge Ordering Induced Ferromagnetic Insulator: $\text{K}_2\text{Cr}_8\text{O}_{16}$

Priya Mahadevan* and Abhinav Kumar

Department of Material Science, S. N. Bose National Centre for Basic Sciences, JD-Block, Sector III, Salt Lake, Kolkata-700098, India

Debraj Choudhury and D. D. Sarma

Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore-560012, India

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Usually metallicity accompanies ferromagnetism. $\text{K}_2\text{Cr}_8\text{O}_{16}$ is one of the less common examples of magnetic materials, exhibiting ferromagnetism in the insulating state. Analyzing the electronic and magnetic properties within first principles electronic structure calculations, we find that the doped electrons due to K induce a charge-ordered and insulating ground state and interestingly also introduce a ferromagnetic coupling between the Cr ions. The primary considerations driving the charge ordering are found to be electrostatic ones with the charge being localized on two Cr atoms that minimize the electrostatic energy. The structural distortion that accompanies the ordering gives rise to a rare example of a charge-order driven ferromagnetic insulator.

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The undoped $3d$ transition metal oxides represent prototypical examples of strongly correlated systems, and they are usually insulators [1]. Ferromagnetic (FM) members are rare, as ferromagnetism is usually accompanied by metallicity [2]. CrO_2 is an example of a FM metal [3]. The mechanism of ferromagnetism is believed to be of double exchange type arising from the presence of both localized and itinerant d electrons [4]. However, the double exchange mechanism and its variants require or imply metallicity. Hence, when one finds an insulating ferromagnet, one must look elsewhere to explain the mechanism. A recently synthesized compound, $\text{K}_2\text{Cr}_8\text{O}_{16}$, is reported [5] to have a FM ordering temperature (~ 180 K), higher than the supposedly metal-to-insulator (MIT) transition temperature (~ 95 K), suggesting a metallic ferromagnet for $95 < T < 180$ K and an insulating ferromagnet for $T < 95$ K, with the latter as the ground state. This compound can be viewed as the 25% K doped analogue of a polymorph of CrO_2 . Thus, introducing a non-integral number of 0.25 electrons per CrO_2 unit, one obtains an insulating ground state, which is also FM.

The first question that comes to mind is whether or not we are working in the realm of experimental uncertainties and the stoichiometric compound is actually metallic in the ground state. Then the consequent ferromagnetism is not a puzzle any more. Recent first principles calculations [6] have examined the electronic and magnetic properties of this compound. In contrast to experiments [5], they find that the ground state is a half-metallic ferromagnet with the Fermi level crossing the majority spin band, while the down spin band has a semiconducting gap. They have examined the formation of an incommensurate long wavelength charge density wave and they do find two parallel one-dimensional Fermi surfaces. Calculation of the non-interacting susceptibility reveals a maximum at q_z^* of $0.295^* \pi/c$ and $1.705^* \pi/c$ at $q_x = 0$ and $q_y = 0$, with

some deviations as a function of q_x and q_y , consistent with the possibility of the formation of an incommensurate charge density wave. There are reports of analogous compounds in the literature. $\text{K}_2\text{V}_8\text{O}_{16}$ [7] exhibit a similar transition from a low temperature insulating phase to a high temperature metallic phase. However, here the insulating state is antiferromagnetic (AFM). $\text{Rb}_2\text{Cr}_8\text{O}_{16}$ [7] has been found to be semiconducting with a T_c which is 90 K higher than the K doped counterpart.

The oxygen positions are usually not determined accurately enough by usual x-ray diffraction, especially when large unit cells are involved [8]. We carried out first principles electronic structure calculations starting with the experimental structure [5], but allowing for structural relaxations, breaking all symmetry constraints. K behaves like a perfect donor in this system, introducing states around 6–8 eV above the Fermi level. The doped electrons go on to occupy the predominantly Cr d bands. The unit cell has eight Cr atoms, and one would expect the doped electrons to be equally distributed. Instead, we find that the two doped electrons are more localized on two Cr sites, the choice driven primarily by electrostatic considerations. The localization is brought about by a polaronic distortion of the surrounding CrO_6 octahedra. As a result of the lowering of the symmetry, one finds that there are unoccupied levels on the Cr atoms neighboring the one which has the localized electron, for the electron to hop to. Energy considerations make this process more favorable for a FM arrangement of spins.

We have carried out first principles electronic structure calculations for $\text{K}_2\text{Cr}_8\text{O}_{16}$ within a plane wave pseudo-potential implementation of density functional theory using projected augmented wave potentials [9] within VASP [10]. The generalized gradient approximation (GGA) [11] was used for the exchange, and electron correlations were considered by including a Hubbard U of 4 eV on Cr (unless

otherwise stated) within the GGA + U formalism [12]. For the closely related polymorph of CrO_2 , a U of at least 3 eV was required [4] to get the experimentally observed half-metallic state. Calculations in the absence of U were also performed for comparison. The self-consistency was performed with a Monkhorst pack k -points grid of 4^*4^*4 . We allowed for atomic relaxations to find the minimum energy configuration. The networks of the Cr atoms in one unit cell and across unit cells are shown in Figs. 1(a) and 1(b), respectively. A cutoff energy of 400 eV was used for the plane wave basis states. Total energies for FM as well as AFM [Figs. 1(c) and 1(d)] configurations were calculated. The density of states were calculated using the tetrahedron method, considering spheres of radii of 1.0 for K, Cr, and O, respectively.

$\text{K}_2\text{Cr}_8\text{O}_{16}$ belongs to a family of oxides called hollandite [5], which have a tunnel running through the unit cell in the z direction. These represent a family of compounds with the general formula $A_xB_8O_{16}$, where A represents large tunnel ions such as Na, K, Ba, Sr, Rb, and Cs and B represents cations in an oxygen octahedron such as Mn, Ti, Al, Cr, V, and Si. The basic network of the Cr atoms in a unit cell [x - y plane] is shown in Fig. 1(a) [Fig. 1(b)]. It consists of two planes of Cr atoms, the dark circles corresponding to the Cr atoms lying in the topmost plane and the lighter circles corresponding to those which lie in the lower plane. Any Cr atom of the top plane has as its neighbors two Cr atoms from the lower plane. Of the two Cr atoms, one is linked to the Cr of the top plane through an edge-shared oxygen (O1) octahedron, while the other is through a corner-shared oxygen octahedron. As a result the distance between one pair of Cr atoms is 2.92 Å [connected by lines in Fig. 1(a)], while that between the other is

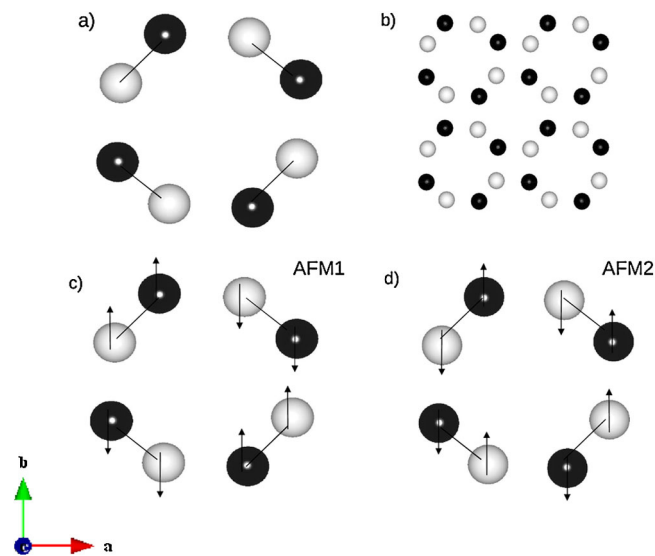


FIG. 1 (color online). The network of Cr atoms in the $z = 0$ plane (black circles) and $z = 0.5$ (white circles) in (a) one unit cell and (b) in the xy plane. The spin arrangements in one unit cell for (c) AFM1 and (d) AFM2 configurations have been shown.

3.42 Å. Thus, the structure consists of one-dimensional zigzag chains of Cr-O networks running in the z direction connected by a bridging oxygen (O2). This was probably what motivated the scenario of a Fermi surface nesting driven charge density wave hypothesis. The entire central portion of the structure is like a tunnel running in the z direction, and this is where the K atoms reside.

The atom projected partial density of states for the relaxed structure for a FM arrangement of spins on Cr is given in Fig. 2 for $U = 0$. The optimized (experimental) inequivalent Cr-O bond lengths are 1.87 (1.87), 1.92 (1.91) ($\times 2$), 1.94 (1.93), and 1.98 (1.97) ($\times 2$) Å. The system is found to be half-metallic in our calculations, consistent with the earlier theoretical work [6] but inconsistent with experiments [5]. Examining the density of states we find that the K atoms contribute in the energy interval 6–8 eV above the Fermi level. At the Fermi level (zero of the energy axis) one has primarily states with Cr d character with t_{2g} symmetry and significant O p admixture. Hence, the doped electrons go on to occupy the Cr d states of t_{2g} symmetry. The states with e_g symmetry are found around 3 eV higher. In addition, one finds an exchange splitting of ~ 2 eV of the Cr d states. We have also plotted the contributions from the two types of oxygen in the unit cell.

Structural optimizations carried out within the framework of GGA + U calculations [12] found the system to be insulating [Fig. 3(c)] for $U \geq 3$ eV. While we present all results here with the reasonable choice of $U = 4$ eV, we note that none of the results presented here are critically dependent on the exact choice of the U value. For example, the stability of this specific insulating state over the metallic state is found to be on the order of 20–40 meV for U in the range of 4–4.5 eV. The eight Cr sites present in the unit cell become inequivalent in the insulating state, with the charge being localized on two Cr atoms. This is evident from the inset of Fig. 3(c), where one finds that charge is depleted from one Cr site (labeled Cr^{4+}) and built on the

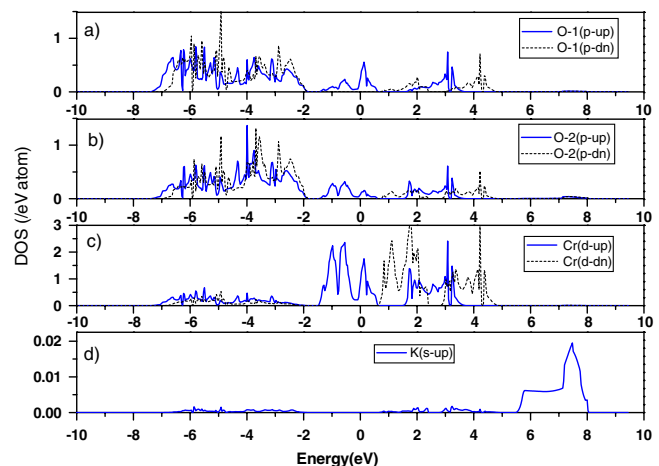


FIG. 2 (color online). The calculated atom and spin projected partial density of states for (a) O1 p , (b) O2 p , (c) Cr d , and (d) K s for $U = 0$. Zero of energy corresponds to the Fermi energy.

other sites labeled Cr^{3+} . This charge ordering is initiated by a structural distortion of the CrO_6 octahedra with the bond lengths being 1.91, 1.92 ($\times 2$), 1.96, and 1.98 ($\times 2$) Å for the Cr^{3+} atom. The Cr^{4+} atom has shorter bond lengths, equal to 1.86, 1.91 ($\times 2$), 1.93, and 1.98 ($\times 2$) with oxygen. The charge difference between the Cr^{3+} and Cr^{4+} sites is, however, only 0.17 electrons in the up spin channel, a much smaller value than the integral valence change expected at the purely ionic limit. A similar deviation from integral valence changes has been observed before in other charge-ordered systems [8]. The structural distortions localize the electron at some Cr sites over others. However, they are not enough to drive the system insulating. Freezing the structure of the system to that obtained by relaxations for a U of 4 eV, we find that, as we vary U from 2 to 4 eV in steps of 1 eV, the system becomes insulating at around 3 eV. Thus, structural distortions in addition to electron correlation effects drive the charge-ordering and the insulating ground state here. The nesting driven charge density wave scenario seems less likely, and a combination of electronic and ionic effects is responsible for the charge-ordered insulating state as in several other examples [13]. Previously, in the context of other systems with large unit cells and low symmetry, it was observed that it is difficult to get good refinements of the oxygen positions from x-ray diffraction alone [8]. We hope that the current work motivates further experiments on this interesting compound.

The next question we asked was, where does the energy gain come from for localizing the electrons when it would seem natural that delocalized electrons would have lower energy? One source of the energy gain comes by minimizing the repulsive electrostatic energy. This is evident from a view of the Cr network shown for the $z = 0$ and $z = 0.5$ planes in Fig. 4(a). Although the two Cr^{3+} atoms on which the electrons are localized are not the farthest in the unit

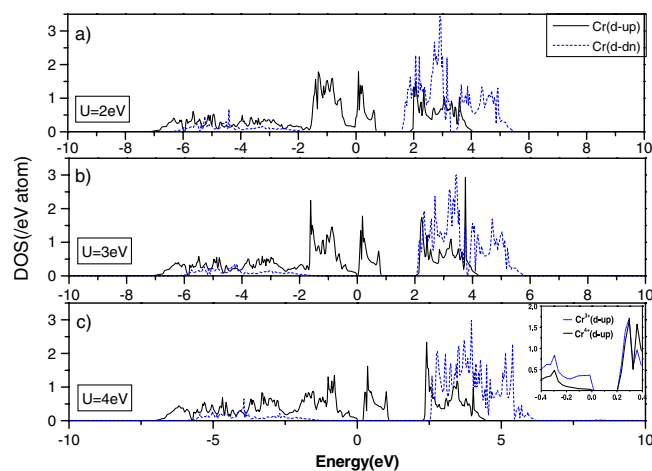


FIG. 3 (color online). The calculated Cr^{3+} d spin projected partial density of states for (a) $U = 2$ eV, (b) $U = 3$ eV, and (c) $U = 4$ eV with the optimized crystal structure of the $U = 4$ eV calculation assumed. Zero of energy corresponds to the Fermi energy. The near Fermi energy region of the up spin Cr^{3+} and Cr^{4+} partial density of states is shown in the inset of (c).

cell, this is the only configuration in which the three-dimensional network has the Cr^{3+} atoms equidistant. Another contribution to the energy gain comes from the intra-atomic exchange interaction (Hund's exchange) obtained when one has increased localization of an electron at an atomic site. It is interesting to note here that the energy difference in the range of 20–40 meV obtained here between the charge-ordered insulating state and the metallic state suggests that any charge order-disorder insulator-metal transition is expected to take place at a temperature above 200 K. This is in contrast to the claim in Ref. [5] indicating a metal-insulator transition at about 95 K.

The entire discussion till now has ignored the magnetism of the underlying lattice. In order to understand whether ferromagnetism should be favored in the insulating state, we start by understanding the origin of the insulating state. The basic energy level diagram of the t_{2g} manifold of the d orbitals is useful for this purpose. We model this within a tight-binding model for a CrO_6 cluster, including Cr d -O p hopping interactions. The hopping interactions vary with Cr-O distance as $1/r^4$ (Harrison's scaling law). In addition, we use single on site energies for Cr d and O p orbitals. Examining the levels comprising the t_{2g} manifold, we find that we have a pair of almost degenerate levels and a singly degenerate level for the experimental Cr-O bond lengths. These levels should hold 2.25 electrons. After the onset of the polaronic distortion, we find that the Cr^{3+} site has longer Cr-O bonds than the experimental structure. As a result the t_{2g} levels move to lower energies as indicated in Fig. 4(b). The Cr-O bond lengths for the Cr^{4+} atoms, however, become shorter, and the singly degenerate level moves to higher energies. We now have a splitting between the highest occupied level on Cr^{3+} and the lowest unoccupied level on the Cr^{4+} site, and so the highest orbital of the t_{2g} manifold is occupied in Cr^{3+} and unoccupied in Cr^{4+} .

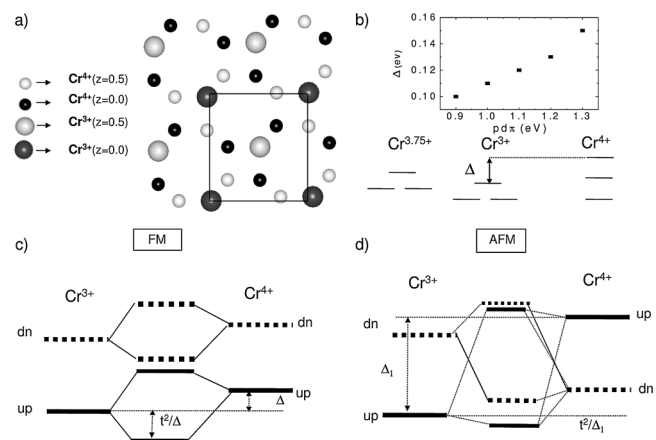


FIG. 4. (a) The network of Cr^{3+} and Cr^{4+} atoms in the $z = 0$ and $z = 0.5$ planes in the unit cell. A schematic level diagram of the splitting of the partially occupied t_{2g} orbitals on Cr^{3+} and Cr^{4+} is given in (b). The energy level diagram for the levels formed by the interaction of Cr^{3+} and Cr^{4+} atoms in (c) FM and (d) AFM arrangements.

TABLE I. Magnetic energies in eV per formula unit.

Configuration	$U = 0$	$U = 4$ eV
FM	0	0
AFM1	0.494	0.553
AFM2	0.312	0.389

Correlation effects should aid an increase in the separation, while solid state effects would broaden the levels into bands. However, the basic picture presented should survive.

Considering just the highest t_{2g} orbital on Cr^{3+} and Cr^{4+} sites, the leftmost and rightmost panels of Figs. 4(c) and 4(d) show the exchange split levels on both atoms. As a result of hopping interaction, these levels interact, forming bonding and antibonding levels, and the central panel represents the level ordering after the interaction for a FM [Fig. 4(c)] and an AFM [Fig. 4(d)] arrangement of spins. There is just one electron in these levels, and so ferromagnetism wins. This is consistent with our calculated results for competing magnetic configurations (Table I). We note that the undistorted lattice without charge ordering leads to a FM metallic ground state, in contrast with the experimental results; the magnetism in such cases would be driven by the double exchange or a Stoner-type mechanism. On the other hand, the magnetism in the insulating state is derived from the FM superexchange interaction, as explained above. This brings us to the experimental claim in Ref. [5], suggesting the existence of a (MIT at ~ 95 K, while the FM order sets in at a considerably higher temperature (~ 180 K). This would require the FM metallic state for $95 < T < 180$ K to have an origin other than the one proposed here, based on the charge-ordered insulating state. In this context, it is interesting to note that there is absolutely no reflection of the MIT at 95 K in the magnetization data (Fig. 1 in Ref. [5]), suggesting that the nature and the origin of the FM order are the same above and below 95 K. In order to resolve this puzzle, we took a closer look at the resistivity data as a function of the temperature (Fig. 3 in Ref. [5]) by magnifying the figure and digitizing the data points. While the data resolution in the reported figure is not of sufficient quality to discuss the $T > 230$ K regime, we find that for $T < 230$ K, the resistivity $\rho(T)$ monotonically increases with decreasing T , suggesting an insulating state for all T less than 230 K and, in particular, at the magnetic ordering temperature of 180 K. In order to understand transport properties further, we analyzed the resistivity data in terms of simple models and found that the low temperature (< 50 K) resistivity is well described by variable-range hopping; this is commonly found in the case of many oxides arising from oxygen vacancies introducing states in the midgap region. The higher temperature (> 100 K) range is easily described as an inhomogeneous system with a macroscopic insulating state with small metallic impurities, presumably arising

from CrO_2 , as reported in Ref. [5]. The band gap of the insulating phase is found to be about 54 meV.

This is in good agreement with our electronic structure calculation with $U = 4$ eV, exhibiting a band gap of ~ 160 meV [see the inset of Fig. 3(c)]. In fact, a combination of these two models, one for the low T regime and the other for the high T regime, is able to describe almost all parts of the transport data well, indicating the macroscopic system to be a gapped insulator with low density of in-gap states arising from inevitable oxygen vacancies with some clusters of metallic impurity. It appears that there is a slightly more rapid change in the transport data around 95 K, as already noted in Ref. [5], but the small deviation from the above-mentioned model description of transport in this system would suggest that this is most likely due to a minority phase and is not an intrinsic property of the stoichiometric compound, thereby establishing a charge-ordered, insulating ferromagnet in a nominally fractionally doped transition metal oxide.

To conclude, we have studied a system where doping of electrons leads to the localization of electrons on two of the eight equivalent Cr atoms present in the unit cell. An unusual polaronic distortion that takes place about some Cr sites brings about this localization, leading to a unique charge ordering. This charge ordering is crucial for ferromagnetism in this material. This gives rise to a rare example of a charge-ordered insulating FM ground state for this remarkable system.

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*Corresponding author.

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