CrO_2: A Self-Doped Double Exchange Ferromagnet

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With the help of band structure calculations $(\mathrm{LSDA} + U)$ a clear picture of the physics behind the metallic ferromagnetic properties of CrO_2 is revealed. It is concluded that CrO_2 is a negative charge transfer gap material which leads to self-doping and explains why it is a metal in spite of the large Coulomb interactions. We find that there exist in CrO_2 both localized and itinerant d electrons, resulting in ferromagnetic ordering due to double exchange similar to colossal magnetoresistance manganates. [S0031-9007(98)06035-9]

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There has been a revival in interest in $3d$ transition metal oxides during the last decade. This was initially stimulated by the discovery of high-T_c superconductivity in complex copper oxides, and more recently by the active study of the colossal magnetoresistance manganates (CMR) $La_{1-x}(Ca,Sr)_xMnO_3$. These latter systems in the most interesting composition range are metallic ferromagnets. This is interesting in itself because both metallic behavior and especially ferromagnetism are rare among the oxides: most of them are antiferromagnetic or ferrimagnetic with dominating antiferromagnetic interactions. We need to meet certain special conditions to stabilize ferromagnetism. One of the main mechanisms invoked to explain ferromagnetic ordering in these systems is the double exchange mechanism [1] which typically acts in doped compounds, although it is not the only one [2].

Another very well known material of this class is chromium dioxide, CrO_2, widely used in magnetic recording tapes. In contrast to $La_{1-x}(Ca,Sr)_xMnO_3$, already pure *stoichiometric* CrO_2 is metallic and ferromagnetic. In its formal 4+ valence state Cr has two $3d$ electrons in t_{2g} orbitals which in a simple picture of strong correlations would suggest a Mott insulatinglike ground state with $S = 1$ local moments and most likely antiferromagnetic spin order. This seems to be about as far from the actual observed properties as one can get. Band structure calculation [3], in contrast to many $3d$ transition metal oxides, do give a good description of these properties concluding that CrO_2 is a so-called half metallic ferromagnet [4]. In this Letter we will address the problem as to *why* CrO_2 is metallic in spite of a large Coulomb interaction. We conclude that the very unique band structure with an almost pure oxygen $2p$ band crossing the Fermi level is responsible for that and that this causes CrO_2 to be mixed valent much like the doped manganates. CrO_2 therefore belongs to the class of negative charge transfer gap materials in the Zaanen-Sawatzky-Allen (ZSA) scheme [5–7]. Using $\mathrm{LSDA} + U$ method [8] we show that the d bands are divided into two parts: a very weakly dispersing band well below the Fermi level providing localized moments, and strongly dispersing and strongly hybridized d bands crossing the Fermi level. The strong hybridization of these bands dilutes the effect of the on-site d-d Coulomb interaction leading to the metallic behavior coexisting with the presence of localized magnetic moments.

CrO_2 is a ferromagnetic metal with a saturation magnetic moment of $2.00\mu_B$ and a low temperature resistivity with a nearly T^2 temperature dependence [9]. Band structure calculations in LSDA [3] explain this behavior as that of a half-metallic ferromagnet [4] with a gap in the minority spin band resulting in the integral magnetic moment per formula unit in spite of the strong covalency effects. However, the magnetic susceptibility in the paramagnetic phase exhibits a Curie-Weiss–like behavior with a local moment of also $2\mu_B$ indicating that the mechanism for ferromagnetic behavior is not a band (Stoner-like) mechanism. Local moments indicate strong correlation effects, and this was, in fact, suggested by early photoemission data [10] which looked more like those of a semiconductor with a vanishing density of states (DOS) at the Fermi energy and a spin polarization of nearly 100% for binding energies about 2 eV below the Fermi level.

CrO_2 has a rutile structure (space group D_{4h}^{14}: $P4_2/mnm$) in which the unit cell consists of two formula units. The Bravais lattice is tetragonal ($c/a = 0.659\,58$) with a lattice constant of $a = 4.421$ Å [11]. The Cr atoms form a body-centered tetragonal lattice and are surrounded by distorted oxygen octahedra. The octahedra surrounding Cr at the body's center and corner positions differ by a 90° rotation about the c axis (see Fig. 1 where Cr1 and Cr2 atoms are in the corners of the unit cell and Cr3 atom is in the body center position). The simplest CrO_6 cluster calculations show that this kind of distortion of the octahedra (elongation along the c axis) leads to the new natural basis for the t_{2g} orbitals: xy, $(yz + zx)$, and $(yz - zx)$ in a local coordinate system for every

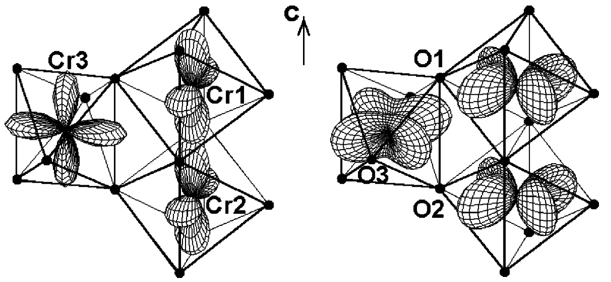

FIG. 1. Angular distribution of xy (left) and ($yz + zx$) (right) electron spin density for the nearest Cr neighbors as determined by LSDA + U. The crystallographic c axis is indicated. The left panel shows the orbitals containing localized spins and the right panel—the more dispersive d orbitals forming bands crossing the Fermi level.

octahedron, in which the z axis is directed to the apex oxygen and the x and y axes are directed to the basal plane oxygens; cf. [12]. Thus in Fig. 1 for Cr3 atom the z axis is directed to the O3 oxygen and the x and y axes are directed to the O1 and O2 oxygens. At the same time, the O1 and O2 become apex oxygens for Cr1 and Cr2, and the z axis is directed to these oxygens. We will demonstrate below that this distorted structure is responsible for rather peculiar properties of the d bands.

LSDA + U calculations were performed in the linearized muffin-tin orbitals (LMTO) approach [13] with atomic spheres radii of 2.06 a.u. for Cr and O and 1.78 and 1.62 a.u. for the two kinds of empty spheres used (8 per unit cell in total) to fill the empty space as much as possible. The spherical harmonics were expanded to the value of $l_{\max} = 3$ and 2 for the atomic and empty spheres, respectively. For the Brillouin zone (BZ) integration 1300 $\mathbf{k}$ points were used. The screened U and J parameters used in the LSDA + U scheme were calculated by constrain method taking into account participation of e_g electrons in screening of the t_{2g} electrons [14] and found to be 3 and 0.87 eV, respectively.

The results of this calculation are shown in Figs. 2–4. First, for $U = 3$ eV the material is found to be a half-metallic ferromagnet, similar to the previous LSDA results [3]. However, inclusion of the electron correlations modifies the electronic structure in a small but nonetheless important way. Together with the shift of the minority spin DOS from the bottom of the conduction band to higher energy, the dip in the majority spin DOS at the Fermi level becomes more pronounced which can be taken as an indication of the tendency toward a gap formation. The decrease of the DOS at E_F in comparison to [3] may be partially responsible for the reduced signal close to E_F observed in photoelectron spectroscopy [10]. In our calculations, however, CrO_2 is still a metal albeit with the reduced DOS at the Fermi level. Note that more recent photoemission data [15] show a finite DOS at E_F, and the spectrum obtained in [15] is in rather good agreement with our calculations.

The tendency to open a gap in an energy spectrum which we noticed above was confirmed by calculation with larger values of U. It was found that the gap would indeed open at $U \geq 6$ eV which would make CrO_2 a Mott-Hubbard insulator.

There are other aspects of the calculation that are very interesting and provide the clues to the basic mechanism for the ferromagnetic metal behavior. First, notice that there are bands of predominantly O $2p$ character crossing the Fermi level close to the Γ point (white and lightly shaded points in Fig. 2). We stress that these are different from the p states which always appear due to d-p hybridization. In our case p states would be present at E_F even with the hybridization switched off (pure p band at the Fermi surface); this is clearly seen from the "coloring" of the bands according to the amount of O $2p$ and Cr $3d$ character as shown in Fig. 2. The fact that almost pure p states extend to the Fermi level is very important. This means that these states can be used as electron or hole reservoirs causing a nonintegral occupation of the d bands. This may be called self-doping [2,7]; it results in Cr becoming actually mixed valent similar to what happens when we dope $LaMnO_3$ by Sr. This is one of the main reasons for the metallic behavior of CrO_2 in spite of quite large U values.

The situation when the almost pure O $2p$ bands cross the Fermi level indicates that such materials should be considered as lying in the negative charge transfer gap region of the ZSA diagram. The negative charge transfer gap behavior is not unexpected for oxides with transition metals in very high oxidation states because of the increased electron affinity of these ions. The crossing of

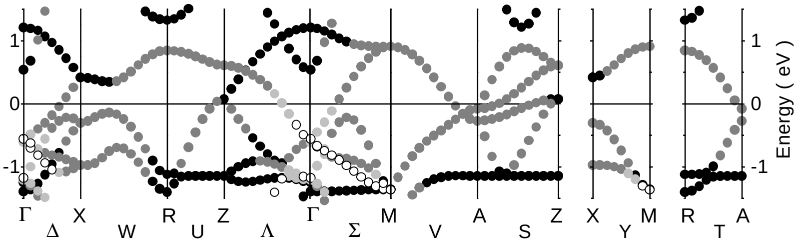

FIG. 2. LSDA + U band structure of CrO_2 for majority spin sublattice in the vicinity of the Fermi level. Open circles denote the contribution of d states less than 25%, light gray circles—between 25% and 50%, gray—between 50% and 75%, and black—predominantly d character of the band. The Fermi level is the zero of energy.

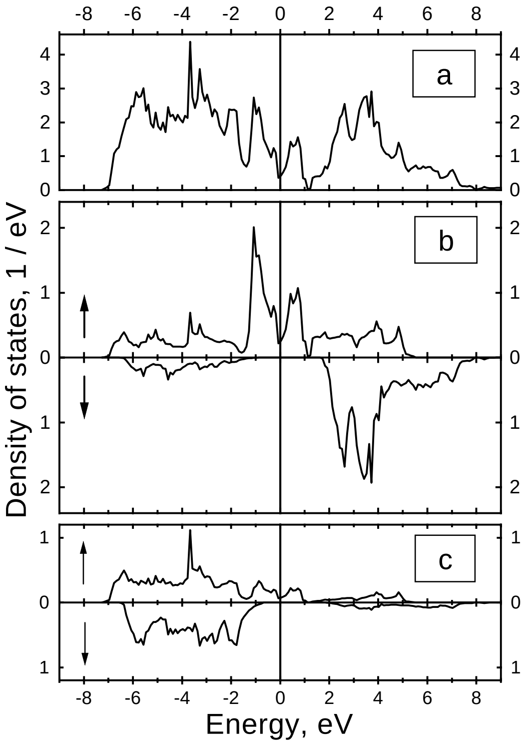

FIG. 3. Total density of states per formula unit and for both spins (a) and partial Cr $3d$ (b) and O $2p$ (c) density of states of CrO_2.

the O $2p$ band of majority spin causes only a magnetic moment on the oxygen which is in qualitative agreement with observation of magnetic x-ray dichroism at the O $1s$ edge in CrO_2 by Schütz *et al.* [16].

Another very important feature is the presence of the almost dispersionless majority spin band at about 1 eV below E_F in Fig. 2 over a large region of the BZ which, as is indicated by the black circles, has almost pure d character. This is observed as a peak in the DOS in Figs. 3 and 4, and corresponds to strongly localized xy orbitals completely occupied by one majority spin electron. Because these states have almost pure d character they are very sensitive to the size of U and shift further away from E_F as U increases.

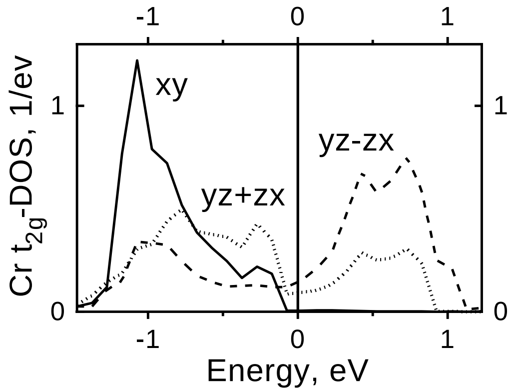

FIG. 4. Partial Cr t_{2g} majority spin density of states in the vicinity of the Fermi level.

On the other hand, the t_{2g} d states (of predominantly $yz + zx$ character at each site) are strongly hybridized with O and form dispersive bands crossing the Fermi level. This explains why the strong d-d Coulomb interaction has relatively little influence on these bands which remain metallic. These electrons move through the core of localized d_{xy} electrons which because of the Hund's rule coupling tend to polarize them, resulting in a ferromagnetic exchange very similar to the double exchange mechanism of Zener [1].

An extra confirmation of this conclusion comes from the calculation, in which we artificially imposed an antiferromagnetic ordering. The simplest two-sublattice antiferromagnetic structure was chosen, with the spin in the body center sites opposite to the spins at the corners of the unit cell. The band structure obtained has a small gap ~ 0.15 eV exactly at the Fermi surface. That means that CrO_2 in an antiferromagnetic phase would have been an insulator. Thus, the metallicity and ferromagnetism in CrO_2 do indeed support each other, in full agreement with the double exchange picture.

The reason for this dualistic behavior of the t_{2g} states, i.e., some localized and others dispersive, can be found in the distortion from an ideal rutile-type crystal structure [17]. Our calculations show that in the ideal structure with the same length of all 12 O–O bonds in a perfect oxygen octahedron, all the t_{2g} bands would have the same width. In the real distorted structure the edge sharing nearest Cr neighbors (Cr1 and Cr2 in Fig. 1) move apart decreasing the xy bandwidth and shifting its center of gravity to low energies in comparison with the centers of gravity of the other two t_{2g} bands. And now with the inclusion of Coulomb interactions, this xy band becomes the first candidate to be fully occupied. Just that happened in our LSDA + U calculation. This picture has much in common with the band structure, proposed by Goodenough [18] on phenomenological grounds.

It is possible to visualize the d orbitals mentioned above (in particular, occupied orbitals) by plotting the angular distribution of d electron spin density for these orbitals (Fig. 1): $\rho(\theta, \phi) = \sum_{m,m'} Q_{m,m'} Y_m(\theta, \phi) Y_{m'}(\theta, \phi)$ where $Q_{m,m'} = n^{\uparrow}_{m,m'} - n^{\downarrow}_{m,m'}$ is the d spin occupation number for the case of xy orbital or 2×2 matrix for the case of $(yz + zx)$ orbital obtained in our self-consistent calculation and $Y_m(\theta, \phi)$ are corresponding spherical harmonics. Note that $(yz + zx)$ orbitals of Cr atoms hybridize with each other via π overlap with O1 and O2 oxygens [12] (right panel of Fig. 1).

From the picture obtained one should expect, as is common for the double exchange systems, a negative magnetoresistance in the paramagnetic region. Previous results have shown that the magnetoresistance of CrO_2 is rather small [9,19], but these measurements were done only below room temperature. It would be interesting to extend these measurements to the region of $T > T_c = 392$ K. As there is no extra "complications" in CrO_2 as compared to CMR manganates (no strong Jahn-Teller effects, no disorder, no formally different valence ions), this study would reveal a pure double exchange contribution to magnetoresistance which, when compared with similar data for manganates, could help to discriminate between the contribution of different mechanisms in the latter.

In conclusion, from the detailed analysis of the obtained LSDA + U band structure a clear physical picture of the electronic structure of CrO_2 is obtained. The strong contribution of the oxygen p states at the Fermi surface explains why this material is a metal and not a Mott insulator in spite of the large U values and the relatively narrow d bands. It also shows that CrO_2 belongs to the class of compounds with negative charge transfer gap leading to a self-doping. It is demonstrated that there exist in CrO_2 two groups of d electrons with significantly different properties: one of the two d electrons of Cr^{4+} is essentially localized, and another is π bonded with the oxygen p orbitals and forms a partially filled narrow band. The resulting picture may be interpreted as an indication that the ferromagnetism in CrO_2 is due to double exchange mechanism. An extra confirmation of this conclusion comes from the fact that in an antiferromagnetic phase CrO_2 would have been an insulator. In this connection the study of magnetoresistance of CrO_2 in a paramagnetic phase may be of interest.

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