

Double-exchange mechanism for CrO₂

P. Schlottmann

Department of Physics and Center for Materials Research and Technology (MARTECH), Florida State University, Tallahassee, Florida 32306

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Band-structure calculations predict a gap of 1.5 eV in the minority-spin density of states of the half-metallic ferromagnet CrO₂. The magnitude of T_C , the magnons, and the activation gap in the resistivity cannot be explained with this band picture. We propose a double-exchange mechanism for two electrons per Cr site invoking strong Hund's rule correlations and the distortion in the CrO₆ octahedra, which localize one electron into the xy orbital at each Cr site, while the electrons in the xz and yz orbitals are itinerant. The effective exchange interaction naturally leads to a ferromagnetic ground state with low-energy magnon excitations and several branches of excitations separated by energy gaps from the ground state, reducing T_C . Quantum fluctuations suppress the orbital long-range order, giving rise to an orbital resonant valence bond-type ground state.

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I. INTRODUCTION

Chromium dioxide, CrO₂, is a half-metallic ferromagnet that is widely used in magnetic recording tapes. A half-metallic ferromagnet¹ is fully spin polarized with the majority-spin component having a Fermi surface and behaving like a metal, while the spectrum of the minority-spin bands is gapped (insulating properties). The full spin polarization makes this compound an ideal candidate for a source of spin-polarized electrons for spin injection into semiconductors at low temperature.²

CrO₂ has a rutile structure with the Cr ions forming a tetragonal body-centered lattice.³ Cr⁴⁺ has a closed-shell Ar core and in addition two 3*d* electrons. The Cr ions are at the center of CrO₆ octahedra, so that the 3*d* orbitals are split into a t_{2g} triplet and an excited e_g doublet. With only two 3*d* electrons to be placed, the e_g states are irrelevant and only the t_{2g} orbitals need to be considered. The tetragonal symmetry distorts the octahedra, which in turn lifts the degeneracy of the t_{2g} orbitals into a xy ground state and $xz+yz$ and $xz-yz$ excited states.^{4,5} Due to the strong correlations in the 3*d* shell the spins of the two 3*d* electrons are aligned to form $S=1$ at each Cr site (first Hund's rule). Hence, the xy orbital is occupied by one electron and to first approximation the xz and yz orbitals have each a 50% probability of being occupied.⁴

The band structure of CrO₂ was calculated by several authors using the local spin density approximation^{4,6-8} (LSDA) and LSDA + U .⁵ In all cases the hybridization of the Cr 3*d* electrons with the O 2*p* states yields a half-metallic ferromagnetic ground state, i.e., the Fermi level is pinned by relatively narrow bands (of widths less than 1 eV) of the majority electrons, and the minority-spin component is gapped at the Fermi level with the O 2*p* states filled and well below the Fermi level, while the Cr 3*d* states are empty and far above the Fermi level. The magnitude of the gap of the minority states depends on the calculation, but it is always at least 1.5 eV.

Experimentally, CrO₂ has a ferromagnetic Curie tempera-

ture T_C in the range of 385–400 K.^{9,10} The magnetic moment, extrapolated to 0 K and high field, is an integral $2.0\mu_B$ per Cr ion. The full spin polarization of CrO₂ at low T has been confirmed recently by tunneling experiments through an Al/I/CrO₂ interface, where I is an artificial barrier and Al acts as the superconducting counterelectrode.¹¹ The temperature dependence of the magnetization well below T_C was found to follow the $T^{3/2}$ dependence expected for ferromagnetic magnons with an average spin-wave stiffness constant of $D=1.8\times 10^{-40}$ Jm².¹⁰ The resistivity has a T^2 variation at low temperatures¹² and at intermediate T it is well described by an Arrhenius law with an activation energy of about 90 K.⁹ The low-temperature specific heat is proportional to T with an enhanced γ coefficient of about 7 mJ K⁻².¹³ The $T^{3/2}$ magnon contribution is also observed in the specific heat.

The activation gap in the resistivity, the $T^{3/2}$ spin-wave dependence of the magnetization, and a T_C of 400 K are not consistent with a gap of 1.5 eV for the minority-spin excitations as predicted by the band-structure calculations. We propose to reconcile this glaring difference in the spin-flip energy by means of many-body correlations (which are not fully included in band calculations) leading to collective low-energy excitations. The origin of the correlations are the Hund's rule coupling and the hopping of the 3*d* electrons (correlated hopping), which gives rise to a ferromagnetic interaction between sites, related to the double-exchange mechanism.¹⁴⁻¹⁶ This mechanism also explains why the ground state of CrO₂ is ferromagnetic in the first place (see also Ref. 5).

The density of states of CrO₂, measured by x-ray and ultraviolet photoemission and bremsstrahlung isochromat spectroscopies,¹³ is in reasonably good agreement with the LSDA + U band calculations (except at low energies),⁵ and the experimental optical conductivity of CrO₂ (Ref. 17) resembles the calculated one.⁸ The above is not unexpected, since the collective double-exchange excitations are not relevant at intermediate and high energies. Many-body aspects and their temperature dependencies have been studied in Refs. 18 and 19 for a two-orbital Hubbard-like model using the dynamical mean-field theory (DMFT) yielding an improved semiquantitative agreement with experiments.

The remainder of the paper is organized as follows. The lattice and electronic structures of CrO_2 are briefly reviewed in Sec. II. Although the O $2p$ orbitals hybridize with the Cr $3d$, we will neglect this effect in this paper, i.e., we assume that the essential correlations arise in the $3d$ shell. In Sec. III we consider the correlated hopping of $3d$ electrons between two neighboring sites including the on-site Hund's coupling. Three situations are discussed. (i) The hopping of electrons in two orbitals per site and the spin degrees of freedom correlated via Hund's rule yields *antiferromagnetically* coupled spins for on average two electrons per site, in analogy to the t - J model, which is the large U limit of the Hubbard model. This case cannot lead to a ferromagnetic ground state. (ii) The xy orbital has lower energy than the xz and yz levels^{4,5} and localizes one electron. An additional electron is allowed to hop between the sites subject to Hund's rule correlations, leading to the well-known double-exchange mechanism, originally introduced to explain the *ferromagnetic* coupling in the manganites.¹⁴⁻¹⁶ (iii) The two-site problem with exactly four electrons, with one localized at each site and the other two exchanged by correlated hopping, again yields a *ferromagnetic* coupling between the sites. Two different orbital states (xz and yz) are necessary for this mechanism. In addition, the coupling between the sites also yields excited states with an energy that is a fraction of the ground-state energy of the Heisenberg ferromagnet. In Sec. IV we briefly discuss the consequences of the coupling on a lattice of spins. A double exchange as the origin of the ferromagnetism of CrO_2 is also suggested in Refs. 5 and 18. The ferromagnetism is accompanied by no long-range order in the orbital states, which form a liquid of resonant valence bonds. A discussion follows in Sec. V.

II. ELECTRONIC STRUCTURE

CrO_2 crystallizes in a rutile structure with two formula units per unit cell.³ The underlying Bravais lattice is body-centered tetragonal with lattice constants $a=b=4.419 \text{ \AA}$, and $c=2.912 \text{ \AA}$.²⁰ The tetragonal symmetry orthorhombically distorts the CrO_6 octahedra. In a unit cell the Cr atoms are then located at the positions $[0,0,0]$ and $[\frac{1}{2}, \frac{1}{2}, \frac{1}{2}]$ in the lattice coordinates, and the four oxygens are placed at $[u, u, 0]$, $[1-u, 1-u, 0]$, $[\frac{1}{2}+u, \frac{1}{2}-u, \frac{1}{2}]$, and $[\frac{1}{2}-u, \frac{1}{2}+u, \frac{1}{2}]$, where $u=0.303$. The shortest distance between Cr ions is 2.912 \AA along the c axis. The side-shared octahedra are then arranged in "ribbons" running parallel to the tetragonal c axis.⁴ Adjacent ribbons (corner-shared octahedra) are rotated by 90° . The t_{2g} orbital contained in the plane of the ribbon is called the xy orbital. From the symmetry of the deformed octahedron the other two orbitals are $xz+yz$ and $xz-yz$, where the z axis is perpendicular to the plane of the ribbon (see Fig. 1). The orthorhombic distortion of the CrO_6 octahedra lifts the degeneracy of the t_{2g} levels with the xy orbital having lowest energy. The $xz+yz$ and $xz-yz$ levels are also split, but with the solid-state effects both have a finite density of states at the Fermi level. For simplicity we will consider these two levels as degenerate throughout the paper.

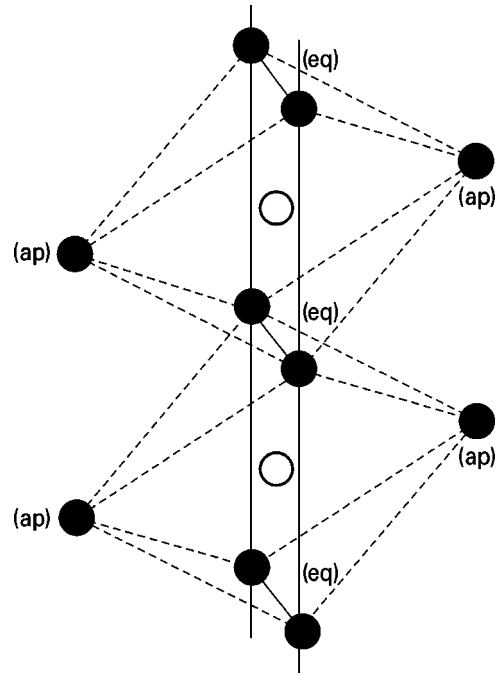


FIG. 1. Cr ion surrounded by the six oxygen atoms forming the octahedron. The octahedra are arranged in "ribbons." The tetragonal symmetry of the lattice distorts the octahedra. The solid lines join neighboring oxygen sites in the equatorial plane, while the dashed lines join the apical (ap) and equatorial (eq) oxygens.

Several LSDA band-structure calculations have been carried out for CrO_2 . Schwarz⁶ predicted a full $2\mu_B$ per Cr^{4+} ion as required by Hund's rules. The Fermi level lies in a partially filled majority (up-spin) band, but the minority (spin-down) density of states is gapped at the Fermi level (gap $\approx 1.5 \text{ eV}$), yielding a half metallic ferromagnet.¹ Similar results were obtained in Ref. 7. A more detailed LSDA calculation by Lewis *et al.*⁴ had a similar outcome (half-metal with a minority gap of about 1.5 eV). The spin-density contour levels revealed a clover-leaf xy pattern for the polarization in the equatorial plane of almost exclusively localized $3d$ character corresponding to $1\mu_B$, while similar results with half the strength were obtained for the xz and yz orbitals.

A slightly different picture was obtained within the framework of a LSDA + U calculation.⁵ The additional Hubbard-like interaction reincorporates some of the correlations normally underestimated or neglected in the LSDA. Again a half-metallic ferromagnet was obtained, but with an enhanced gap (of about 2.7 eV for $U=3 \text{ eV}$) in the minority-spin density of states. There was also a stronger participation of the O $2p$ states at the Fermi level in the majority band. Korotin *et al.*⁵ proposed CrO_2 to be a self-doped double-exchange ferromagnet. If U was increased further ($U > 6 \text{ eV}$) a gap opened as well in the majority band.

III. EXCHANGE MECHANISMS

In this section we consider the hopping of the $3d$ electrons between two Cr sites subject to the on-site correlations leading to Hund's rules. The correlations and the hopping

yield an effective exchange interaction between the sites. In order to simplify the problem to the essential features, we introduce the following approximations: (i) Although the hopping between sites is mediated by the oxygen $2p$ states, here we will assume direct hopping between Cr sites. (ii) We assume that the hopping is diagonal in the orbital index. This hypothesis has no consequences for the two-site problem, since we may diagonalize the hopping matrix and define a new basis of orbital states. (iii) We assume the hopping matrix element is the same for all orbital channels, but it may be spin dependent.

Three situations are considered in this section: (A) The hopping of correlated electrons in two orbitals with on average two electrons per site, which gives rise to antiferromagnetic coupling, (B) one localized electron per site in the xy orbital and one electron hopping between the sites (ferromagnetic double-exchange mechanism¹⁴⁻¹⁶), and (C) the two-site problem with exactly four electrons, one being localized at each site and the other two electrons allowed to hop, which again leads to ferromagnetic coupling. We limit ourselves to derive the exchange interaction between sites, which gives rise to the magnetic excitations, and project out all other degrees of freedom.

A. Hopping of electrons in two orbitals

For two orbitals, α and β , the subspace for two electrons at a site consists of six states, namely, the direct product of the spin triplet times the orbital singlet and the spin singlet times the orbital triplet. Hund's rule coupling of strength $U > 0$ reduces the energy of the spin triplet to $-U$ and increases the energy of the spin singlet to U . The ground state at site j is then one of the following states:

$$\begin{aligned}\psi_{j+} &= c_{j\alpha\uparrow}^\dagger c_{j\beta\uparrow}^\dagger |j0\rangle, \\ \psi_{j0} &= 2^{-1/2}(c_{j\alpha\uparrow}^\dagger c_{j\beta\downarrow}^\dagger + c_{j\alpha\downarrow}^\dagger c_{j\beta\uparrow}^\dagger) |j0\rangle, \\ \psi_{j-} &= c_{j\alpha\downarrow}^\dagger c_{j\beta\downarrow}^\dagger |j0\rangle,\end{aligned}\quad (1)$$

where $c_{jm\sigma}^\dagger$ creates an electron in the orbital m with spin σ , and $|j0\rangle$ denotes the vacuum state at site j .

For the two-site problem we restrict ourselves to the subspace of nine states spanned by the on-site spin-triplet/orbital-singlet states. Due to the rotational invariance of the spin space, the nine states can be classified according to the total spin, i.e., $S=0, 1$, and 2 , and the spin projection along the z direction. Denoting the two sites 1 and 2, the hopping of electrons between the sites with amplitude t is given by $H_t = -t \sum_{\sigma} (c_{1\alpha\sigma}^\dagger c_{2\alpha\sigma} + c_{2\alpha\sigma}^\dagger c_{1\alpha\sigma} + c_{1\beta\sigma}^\dagger c_{2\beta\sigma} + c_{2\beta\sigma}^\dagger c_{1\beta\sigma})$. The hopping Hamiltonian applied to the states $\psi_{1+}\psi_{2+}$ or $\psi_{1-}\psi_{2-}$ yields zero. These states are part of the $S=2$ quintuplet, which has energy $-2U$, due to the absence of dynamics. The remaining three states of the $S=2$ multiplet are obtained by successively applying the spin-lowering operator to the state $\psi_{1+}\psi_{2+}$, e.g. for $S_z=1$ we obtain $2^{-1/2}(\psi_{10}\psi_{2+} + \psi_{1+}\psi_{20})$.

The state with $S_z=1$ orthogonal to the above $S=2$ state is $2^{-1/2}(\psi_{10}\psi_{2+} - \psi_{1+}\psi_{20})$, which has total spin $S=1$. The re-

duction of the energy of the $S=1$ states due to hopping is $-2U - 4t^2/U$ to second order in t . The remaining two states of this multiplet are obtained by applying the spin-lowering operator. There are altogether three states with spin projection $S_z=0$. One state belongs to the $S=2$ multiplet, a second state to the $S=1$ triplet, and the third state has total spin $S=0$. This state can easily be obtained from the orthogonality condition to the other two states, i.e. $3^{-1/2}(\psi_{1-}\psi_{2+} + \psi_{1+}\psi_{2-} - \psi_{10}\psi_{20})$. To second order in t the energy of this state is $-2U - 6t^2/U$.

The effective Hamiltonian for the two-site subspace under consideration is

$$H_{eff} = -2U - 2(t^2/U)(1 - \mathbf{S}_1 \cdot \mathbf{S}_2), \quad (2)$$

where \mathbf{S}_j are the effective $S=1$ operators at site j . Here the spin operators contain the components of both orbital degrees of freedom, i.e., $\mathbf{S}_j = \mathbf{s}_{j\alpha} + \mathbf{s}_{j\beta}$. The effective coupling between the spins is *antiferromagnetic*, in analogy to the spin-spin coupling in the t - J model,^{21,22} and cannot give rise to *ferromagnetism* in CrO₂. Note that this model is different from the standard t - J model, which involves spin- $\frac{1}{2}$ operators and no Hund's rule coupling.

For a given state the amount of the reduction depends on the dynamics of the electrons under hopping. The $S=2$ states have no dynamics, while the possibilities for hopping are maximum for the $S=0$ state, i.e., the spin polarization inhibits the hopping of the electrons. This situation is qualitatively unchanged if a third orbital channel is included, which increases the number of possible wave functions and hence the amount of algebra. The main conclusion, i.e., antiferromagnetic coupling of the spins, remains unchanged.

B. Double exchange

The conclusion of Sec. III A (antiferromagnetic coupling) completely changes if there is a localized spin at each site. Hund's rule couples the spin of the localized electron with that of the itinerant electrons and the hopping becomes correlated, i.e., it now depends on the relative z projections of the localized spins and that of the conduction electron. This mechanism is known as the double exchange and was originally proposed to explain the ferromagnetic phase in the manganites.¹⁴⁻¹⁶

As argued in Sec. II due to the tetragonal symmetry the xy orbital has lowest energy and contains one localized electron. We consider the simplest situation leading to double exchange, and assume a localized spin \vec{S} at each Cr site and only one orbit for the itinerant electrons. The hopping between the sites labeled 1 and 2 is then

$$\begin{aligned}H_{hop} &= -t \sum_{S_{1z} S_{2z} \sigma} (\vec{S} S_{1z} + \frac{1}{2} \sigma | \vec{S} \frac{1}{2} (\vec{S} + \frac{1}{2}) (S_{1z} + \sigma) \\ &\quad \times (\vec{S} S_{2z} + \frac{1}{2} \sigma | \vec{S} \frac{1}{2} (\vec{S} + \frac{1}{2}) (S_{2z} + \sigma) \\ &\quad \times (c_{1\sigma}^\dagger c_{2\sigma} + c_{2\sigma}^\dagger c_{1\sigma}),\end{aligned}\quad (3)$$

where the symbols in parentheses denote Clebsch-Gordan coefficients enforcing Hund's rules at each site. For one localized electron per site we have $\tilde{S}=\frac{1}{2}$, while for two localized electrons then $\tilde{S}=1$, etc. For $\tilde{S}=\frac{3}{2}$ the model represents the situation of Mn^{3+} and Mn^{4+} of the manganites.²³ Note that the localized electrons do not participate in hopping.

For $\tilde{S}=\frac{1}{2}$ the states of the two-site problem can be classified into a pair of $S=\frac{3}{2}$ quadruplets and a pair of $S=\frac{1}{2}$ doublets. The two states with full spin polarization are

$$\psi_{\pm}^{3/2}=2^{-1/2}(c_{1\uparrow}^{\dagger}\pm c_{2\uparrow}^{\dagger})|1\uparrow,2\uparrow\rangle, \quad (4)$$

where the ket contains the spin components of the two localized electrons at sites 1 and 2, respectively. These two states are eigenstates of the hopping Hamiltonian. Since the Clebsch-Gordan coefficients for this case are equal to one, the energy of the states is $\mp t$. The state with lower energy corresponds to the bonding state, while the one with higher energy is the antibonding state. Due to the spin rotational invariance all four states of the bonding quadruplet have energy $-|t|$ and all states of the antibonding quadruplet have energy $|t|$. The remaining states of the quadruplets are obtained by successively applying the total spin-lowering operator to the states (4).

The bonding and antibonding $S=\frac{1}{2}$ doublet states are constructed using the orthogonality to the quadruplet states. They are, of course, also eigenstates of the hopping Hamiltonian (3). For the spin projection $+\frac{1}{2}$ these states are

$$\begin{aligned} \psi_{\pm}^{1/2} &= (12)^{-1/2}(c_{1\uparrow}^{\dagger}|1\uparrow,2\uparrow\rangle + c_{1\uparrow}^{\dagger}|1\downarrow,2\uparrow\rangle \pm c_{2\downarrow}^{\dagger}|1\uparrow,2\uparrow\rangle \\ &\quad \pm c_{2\uparrow}^{\dagger}|1\uparrow,2\downarrow\rangle) + 3^{-1/2}(c_{1\uparrow}^{\dagger}|1\uparrow,2\downarrow\rangle \pm c_{2\uparrow}^{\dagger}|1\downarrow,2\uparrow\rangle), \end{aligned} \quad (5)$$

which have energy $\pm\frac{1}{2}t$. The factor $\frac{1}{2}$ in the energy arises from the Clebsch-Gordan coefficients. The remaining two states are obtained by reversing all spins.

The results for $\tilde{S}=\frac{1}{2}$ can then be summarized as follows. The ground state belongs to the bonding multiplet with largest total spin. Hence, the spins are all *ferromagnetically* coupled with each other, as expected for the double-exchange mechanism. For the generalization to arbitrary \tilde{S} (see, e.g., Ref. 23) the ground state again belongs to the bonding multiplet of maximum spin and has energy $-|t|$, such that the sites are also *ferromagnetically* correlated. Orbital degrees of freedom do not affect this result.

C. Double exchange for CrO_2

We assume that at both sites the xy orbital is occupied with one electron and that there are two itinerant electrons in two orbitals (xz and yz). The Hund's rule locally couples all spins ferromagnetically. As in Sec. III A we denote the orbitals by α and β . The localized electron of spin component s at site j is denoted by the ket $|js\rangle$. The relevant spin-triplet states with orbital α at site j are now

$$\begin{aligned} \varphi_{j\alpha+} &= c_{j\alpha\uparrow}^{\dagger}|j\uparrow\rangle, \\ \varphi_{j\alpha 0} &= 2^{-1/2}(c_{j\alpha\uparrow}^{\dagger}|j\downarrow\rangle + c_{j\alpha\downarrow}^{\dagger}|j\uparrow\rangle), \\ \varphi_{j\alpha-} &= c_{j\alpha\downarrow}^{\dagger}|j\downarrow\rangle. \end{aligned} \quad (6)$$

For two orbitals this set of states consists of six states per site.

The hopping of the itinerant electrons changes the configuration with two electrons per site to one in which one site has one (localized) electron and the other site three electrons (one localized and two itinerant). This new state requires a large energy U . To second order in the hopping t we obtain an effective exchange interaction within the space of states spanned by the set (6) in analogy to the procedure shown in Sec. III A. The states can be classified according to the total spin, the total spin projection, and the orbital state (singlet or triplet).

We consider first the states with maximum spin, $S=2$. There are four spin quintuplets, three corresponding to an orbital triplet and one to the orbital singlet. The orbital triplet two-site states are invariant under the exchange of orbital indices (even parity), while the wave function of the orbital singlet state changes sign if the orbital labels are interchanged (odd parity). The spin-polarized states of the orbital triplet are

$$\begin{aligned} \psi_{even}^{\alpha\alpha}(S=2) &= c_{1\alpha\uparrow}^{\dagger}c_{2\alpha\uparrow}^{\dagger}|1\uparrow,2\uparrow\rangle = \varphi_{1\alpha+}\varphi_{2\alpha+}, \\ \psi_{even}^{\alpha\beta}(S=2) &= 2^{-1/2}(c_{1\alpha\uparrow}^{\dagger}c_{2\beta\uparrow}^{\dagger} + c_{1\beta\uparrow}^{\dagger}c_{2\alpha\uparrow}^{\dagger})|1\uparrow,2\uparrow\rangle \\ &= 2^{-1/2}(\varphi_{1\alpha+}\varphi_{2\beta+} + \varphi_{1\beta+}\varphi_{2\alpha+}), \quad (7) \\ \psi_{even}^{\beta\beta}(S=2) &= c_{1\beta\uparrow}^{\dagger}c_{2\beta\uparrow}^{\dagger}|1\uparrow,2\uparrow\rangle = \varphi_{1\beta+}\varphi_{2\beta+}, \end{aligned}$$

and the corresponding orbital singlet state is

$$\begin{aligned} \psi_{odd}^{\alpha\beta}(S=2) &= 2^{-1/2}(c_{1\alpha\uparrow}^{\dagger}c_{2\beta\uparrow}^{\dagger} - c_{1\beta\uparrow}^{\dagger}c_{2\alpha\uparrow}^{\dagger})|1\uparrow,2\uparrow\rangle \\ &= 2^{-1/2}(\varphi_{1\alpha+}\varphi_{2\beta+} - \varphi_{1\beta+}\varphi_{2\alpha+}). \end{aligned} \quad (8)$$

It is straightforward to see that the orbital triplet states have no dynamics, because when applied to the hopping Hamiltonian they yield zero. The energy of the state with odd orbital parity, on the other hand, is reduced by the amount $-4t^2/U$. The remaining states (with other spin projections) are generated by successively applying the spin-lowering operator.

The states with total spin $S=1$ and projection $S_z=1$ are constructed using the orthogonality condition to the states with $S=2$ and the same spin projection. Again, there are four such multiplets corresponding to orbital triplet and singlet states, i.e.,

$$\begin{aligned} \psi_{even}^{\alpha\alpha}(S=1) &= 2^{-1/2}(\varphi_{1\alpha 0}\varphi_{2\alpha+} - \varphi_{1\alpha+}\varphi_{2\alpha 0}), \\ \psi_{even}^{\alpha\beta}(S=1) &= 2^{-1}(\varphi_{1\alpha 0}\varphi_{2\beta+} - \varphi_{1\alpha+}\varphi_{2\beta 0} \\ &\quad + \varphi_{1\beta 0}\varphi_{2\alpha+} - \varphi_{1\beta+}\varphi_{2\alpha 0}), \\ \psi_{even}^{\beta\beta}(S=1) &= 2^{-1/2}(\varphi_{1\beta 0}\varphi_{2\beta+} - \varphi_{1\beta+}\varphi_{2\beta 0}), \end{aligned}$$

$$\begin{aligned} \psi_{odd}^{\alpha\beta}(S=1) = & 2^{-1}(\varphi_{1\alpha 0}\varphi_{2\beta+} - \varphi_{1\alpha+}\varphi_{2\beta 0} \\ & - \varphi_{1\beta 0}\varphi_{2\alpha+} + \varphi_{1\beta+}\varphi_{2\alpha 0}), \end{aligned} \quad (9)$$

and all four states have the energy $-2t^2/U$. The states with other spin projections are obtained by successively applying the spin-lowering operator.

The four spin-singlet states ($S=0$) are again obtained via orthogonality to the other states:

$$\begin{aligned} \psi_{even}^{\alpha\alpha}(S=0) = & 3^{-1/2}(\varphi_{1\alpha+}\varphi_{2\alpha-} + \varphi_{1\alpha-}\varphi_{2\alpha+} - \varphi_{1\alpha 0}\varphi_{2\alpha 0}), \\ \psi_{even}^{\alpha\beta}(S=0) = & 6^{-1/2}(\varphi_{1\alpha-}\varphi_{2\beta+} + \varphi_{1\alpha+}\varphi_{2\beta-} - \varphi_{1\alpha 0}\varphi_{2\beta 0} \\ & + \varphi_{1\beta-}\varphi_{2\alpha+} + \varphi_{1\beta+}\varphi_{2\alpha-} - \varphi_{1\beta 0}\varphi_{2\alpha 0}), \\ \psi_{even}^{\beta\beta}(S=0) = & 3^{-1/2}(\varphi_{1\beta+}\varphi_{2\beta-} + \varphi_{1\beta-}\varphi_{2\beta+} - \varphi_{1\beta 0}\varphi_{2\beta 0}), \\ \psi_{odd}^{\alpha\beta}(S=0) = & 6^{-1/2}(\varphi_{1\alpha-}\varphi_{2\beta+} + \varphi_{1\alpha+}\varphi_{2\beta-} - \varphi_{1\alpha 0}\varphi_{2\beta 0} \\ & - \varphi_{1\beta-}\varphi_{2\alpha+} - \varphi_{1\beta+}\varphi_{2\alpha-} + \varphi_{1\beta 0}\varphi_{2\alpha 0}), \end{aligned} \quad (10)$$

and the energies are $-3t^2/U$ for the orbital triplet and $-t^2/U$ for the orbital singlet.

The state with lowest energy is then the orbital singlet with $S=2$, indicating that in the ground state the system favors *ferromagnetic* coupling. The energies for all the states of the two-site molecule can be cast into the following expression:

$$H_{12}^{eff} = -2(t^2/U)[(\frac{3}{4} - \boldsymbol{\tau}_1 \cdot \boldsymbol{\tau}_2) - (\frac{1}{4} + \boldsymbol{\tau}_1 \cdot \boldsymbol{\tau}_2)\mathbf{S}_1 \cdot \mathbf{S}_2], \quad (11)$$

where $\boldsymbol{\tau}_j$ are the ‘‘spin- $\frac{1}{2}$ ’’ operators for the orbital pseudospin at site j , and \mathbf{S}_j are the spin operators for the total spin $S=1$ at site j .

IV. THE CrO₂ LATTICE

In this section we discuss the consequences of the double-exchange mechanism for CrO₂.

(i) From the cases discussed in Sec. III we conclude that the two-site interaction only favors ferromagnetism if there is a localized spin at each site. An electron can only be localized if the degeneracy of the t_{2g} levels is lifted. Hence, the strong distortion of the octahedra, a consequence of the tetragonal symmetry, is crucial for the ferromagnetic half-metallic ground state of CrO₂.

(ii) The effective Hamiltonian for the lattice is the sum of Eq. (11) over all the pairs of neighboring sites, i.e.,

$$H^{eff} = -2 \sum_{\langle ij \rangle} (t_{ij}^2/U)[(\frac{3}{4} - \boldsymbol{\tau}_i \cdot \boldsymbol{\tau}_j) - (\frac{1}{4} + \boldsymbol{\tau}_i \cdot \boldsymbol{\tau}_j)\mathbf{S}_i \cdot \mathbf{S}_j], \quad (12)$$

where t_{ij} depends on the distance between the sites. For the ferromagnetic ground state the Hamiltonian reduces to an effective Heisenberg model for the orbital degrees of freedom,

$$H^{eff} = -2 \sum_{\langle ij \rangle} (t_{ij}^2/U)(\frac{1}{2} - 2\boldsymbol{\tau}_i \cdot \boldsymbol{\tau}_j). \quad (13)$$

(iii) We now analyze the possibility of (antiferro-)orbital long-range order in the ground state due to Eq. (13). The situation is simplest for interpenetrating sublattices, e.g., for interactions between nearest-neighbor sites on different ribbons. The natural sublattices for a body-centered tetragonal lattice are the corners of the tetragon and body-centered sites. If one of the sublattices orders in the orbital α and the other sublattice orders in β , the ground-state energy is $-Nzt^2/U$, where N is the number of sites and z the coordination number (in this case $z=8$). This energy is higher (less favorable) than expected from the two-site problem because the orbital long-range order suppresses the hopping between sites. Orbital singlets can no longer be formed between all nearest-neighbor sites simultaneously. Interchanging one pair of orbitals on nearest-neighbor sites between the orbitally ordered sublattices introduces $2(z-1)$ ‘‘wrong’’ bonds. Such an excitation of energy $4(z-1)t^2/U$ is induced by the orbital-flip operators in Eq. (13), i.e., $(\tau_i^+ \tau_j^- + \tau_i^- \tau_j^+)$, and in second-order perturbation it reduces the ground-state energy by a factor $[1 + 0.5(z-1)^{-1}]$, which for $z=8$ is a decrease of 7%. The energy can be reduced further by switching the orbitals at more than one link. Hence, the mean-field state with long-range antiferro-orbital order is not the one of lowest energy, i.e., quantum fluctuations are of fundamental importance.

(iv) Assuming that the hopping matrix element is a rapidly decreasing function of the distance, we will consider only nearest- and next-nearest-neighbor sites. The shortest distance between Cr sites is along the c axis, i.e., the sites lie on the same ribbon. This distance is $d_{nn} = c = 2.912 \text{ \AA}$, while the next-nearest-neighbor sites with $d_{nnn} = \frac{1}{2}\sqrt{c^2 + 2a^2} = 3.447 \text{ \AA}$ are from the body center to a corner of the tetragon. Hence, if only the nearest-neighbor sites are considered, the system consists of chains along the ribbons. The Heisenberg chain has resonant valent bonds (RVBs) but no long-range order. The ground-state energy per RVB link is $-4(t^2/U)\ln 2 \approx -2.8t^2/U$. Within the context of point (iii) nearest-neighbor bonds correspond to interactions within the same sublattice, while next-nearest neighbors link the two sublattices. All interactions are antiferro-orbital and cannot be satisfied simultaneously, so that there is a large orbital frustration. The quantum-mechanical nature of the frustration again hints at a RVB-like state for the orbits, rather than long-range orbital order.

(v) The low-energy magnetic excitations are ferromagnetic magnons, which we treat within the linearized spin-wave approximation (LSWA). The spin operators are parametrized by boson operators a_j and a_j^\dagger , $S_j^+ = (2S - a_j^\dagger a_j)^{1/2} a_j$, $S_j^- = a_j^\dagger (2S - a_j^\dagger a_j)^{1/2}$, and $S_j^z = S - a_j^\dagger a_j$. The spin operators are replaced in the spin Heisenberg Hamiltonian (the orbital degrees of freedom are traced out by taking the ground-state expectation value) and then the Hamiltonian is expanded into a power series of boson operators. Keeping only terms bilinear in boson operators we obtain, after Fourier transforming, the LSWA Hamiltonian

$$H_{LSWA} = -JNS^2 - 4J'NS^2 + \sum_{\mathbf{k}} [4JS \sin^2(k_z c/2) + 8J'S(1 - \gamma_{\mathbf{k}})] b_{\mathbf{k}}^\dagger b_{\mathbf{k}}, \quad (14)$$

where $\gamma_{\mathbf{k}} = 8^{-1} \sum_{\delta} \exp(i\mathbf{k} \cdot \boldsymbol{\delta})$ with $\boldsymbol{\delta}$ representing the eight next-nearest-neighbor sites, J and J' are the nearest- and next-nearest-neighbor exchanges, respectively, and the z direction is chosen along the c axis. Here $b_{\mathbf{k}}^\dagger$ and $b_{\mathbf{k}}$ are the spin-wave boson operators in reciprocal space.

(vi) Expanding the dispersion for small \mathbf{k} we obtain that the magnon stiffness constant is anisotropic, namely, $D_x = D_y = J'Sa^2$ and $D_z = (J+J')Sc^2$. The low- T dependence of the internal energy is $U \propto T^{5/2}$, where the anisotropy only changes the prefactor but not the exponent. The contribution of the magnons to the specific heat is then proportional to $T^{3/2}$, which has to be added to the electronic specific heat (linear in T) and the one of acoustic phonons ($\propto T^3$).¹³ Hence, the electronic specific heat is the dominant term at low T . The magnetization per Cr ion at low T is $S - \alpha T^{3/2}$, where α is a constant that depends on the average stiffness constant. This is in agreement with the experimental observations.

(vii) The excited multiplets studied in Sec. III C are gapped and not populated at very low T . Their magnetic content is less than the ferromagnetic ground state. Hence, since these states are gradually occupied with increasing T , the magnetization has to decrease more quickly than for that of the ordinary Heisenberg model. This could be an explanation for the relatively low Curie temperature ($T_C \approx 400$ K) as compared to the band gap of the minority band. A further implication is that the polarization of CrO_2 [nearly 100% at $T=0$ (Ref. 11)] would rapidly decrease with temperature. CrO_2 is then a less efficient spin-injection source at room temperature than originally expected. The exchange interaction strength associated with T_C is $4t^2/U$.

V. DISCUSSION

LSDA band calculations for the half-metallic ferromagnet CrO_2 predict a gap in the minority-spin density of states that is by far too large to account for the low T_C , ferromagnetic magnons, and the Arrhenius law of the resistivity. To explain discrepancies it is necessary to invoke collective excitations of the spins. Based on the splitting of the t_{2g} multiplet in a distorted CrO_6 octahedron and the local Hund's rule correlations in the $3d$ shells, we constructed an effective double-exchange model involving two electrons per Cr site. Below we summarize and discuss the results, their limitations, and consequences.

(i) To obtain a *ferromagnetic* exchange it is necessary to have a localized orbital per site. The distortion of the octahedra is of crucial importance to localize the xy orbital. A localization would not be possible for CrO_2 in cubic symmetry for which all three t_{2g} orbitals are degenerate and the resulting exchange is antiferromagnetic (see Sec. III A).

(ii) CrO_2 has exactly two electrons per site (one localized in the xy orbital and one itinerant in the xz and yz orbitals). The resulting double-exchange mechanism is then different

from that for manganites (see Secs. III B and III C). It is of fundamental importance that two different orbitals are involved in the hopping, because this allows two itinerant electrons with the same spin projection to temporarily be at the same site. The latter is not essential in the manganites. The double-exchange mechanism could be the reason why CrO_2 is ferromagnetic.⁵

(iii) The effective exchange interaction naturally leads to a ferromagnetic ground state with low-energy long-wavelength magnon excitations. Quantum fluctuations suppress the long-range order of the orbital degrees of freedom. A RVB-type of orbital liquid is expected from this model.

(iv) We considered a diagonal and isotropic hopping between orbitals. This assumption is of course not realistic for CrO_2 . The hopping is mediated by the oxygen $2p$ electrons and is strongly directional. The orbital quantum number is not conserved, i.e., we may hop from an α orbital into a β one. This is not relevant for the two-site problem, which can always be diagonalized, but it is for the many-site case, where all links cannot be diagonalized simultaneously. The hopping also depends on whether it is along a ribbon or between ribbons.

(v) The consequence of directional hopping is that the orbital space no longer consists of singlets and triplets, but of other linear combinations. This will reduce the symmetries of the RVB-like orbital liquid, but quantum frustration is still expected to be present.

(vi) In Sec. III C we obtained an effective interaction between sites with exactly two electrons per Cr ion. Although we considered the dynamics of the electrons, at the end of the calculation we projected onto Hund's rule states with two electrons per site. Strictly speaking this subset of states constitutes an insulator. The interaction Hamiltonian is an essential but only partial aspect of CrO_2 , since it neglects the dynamics of the electrons, which would have to be included in the complete, however, much more complex problem. At this point it is useful to argue that the solid-state effects broaden the levels into bands of finite width. The band broadening may have to be supplemented by "self-doping" from the O $2p$ states,⁵ which yields a mixed-valent state due to hybridization and hence additional band width. These mechanisms would lead to a metal despite large Coulomb interactions.

(vii) We now conjecture about the conductivity. Overlapping bands of finite width lead to a metallic state. In the ferromagnetic ground state all electrons are spin polarized, so that the system is a half metal with finite conductivity. The scattering of the electrons off the spin waves (two-magnon processes) gives rise to a power law with temperature, which was found to be $T^{9/2}$ in Ref. 24. This temperature dependence is difficult to separate from the phonon scattering (T^5). The dominant dependence of $\rho(T)$ at low T is due to the strong Coulomb interactions and is proportional to T^2 . This power law follows from Fermi-liquid arguments for the metallic spin component (i.e., the numbers of available initial and final states in the scattering process are both proportional to T). A possible explanation for the experimentally found exponential activation^{9,10} is that the scattering process could

involve a transition into one of the excited multiplets. The Boltzmann factor of the excited state is then the origin of the temperature dependence.

(viii) T_C is expected to be smaller than that for a standard Heisenberg model, because the several branches of excitations (which have lesser spin content than the ground state) when populated reduce the magnetization. Also the polarization of CrO₂ is reduced with T due to the population of the excited multiplets. CrO₂ is then likely to be a less good spin injector at room temperature than originally expected. A

strong temperature dependence of the density of states has recently been found within the LSDA+DMFT.¹⁹

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