Origins of multi-sublattice magnetism and superexchange interactions in double–double perovskite CaMnCrSbO$_{6}$

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Abstract

The multi-sublattice magnetism and electronic structure in double–double perovskite compound CaMnCrSbO$_{6}$ is explored using density functional theory. The bulk magnetization and neutron diffraction suggest a ferrimagnetic order ($T_{C} \sim 49$ K) between between Mn$^{2+}$ and Cr$^{3+}$ spins. Due to the non-equivalent Mn atoms (labelled as Mn(1) and Mn(2) which have tetrahedral and planar oxygen coordinations, respectively) and the Cr atom in the centre of distorted oxygen octahedron in the unit cell, the exchange interactions are more complex than that expected from a two sublattice magnetic system. The separations between the on-site energies of the $d$-orbitals of Mn(1), Mn(2) and Cr obtained from Wannier function analysis are in agreement with their expected crystal field splitting. While the DOS obtained from non spin-polarized calculations show a metallic character, starting from Hubbard $U = 0$ eV the spin-polarized electronic structure calculations yield a ferrimagnetic insulating ground state. The band gap increases with $U_{eff}(U - J)$, thereby showing a Mott–Hubbard nature of the system. The inclusion of anti-site disorder in the calculations show decrease in band-gap and also reduction in the total magnetic moment. Due to the $\sim 90^\circ$ superexchange, nearest neighbour exchange constants obtained from DFT are an order of magnitude smaller than those reported for various magnetic perovskite and double-perovskite compounds. The Mn(1)–O–Mn(2) (out of plane and in-plane), Mn(1)–O–Cr and Mn(2)–O–Cr superexchange interactions are found to be anti-ferromagnetic, while the Cr–O–O–Cr super-superexchange is found to be ferromagnetic. The Mn(2)–O–Cr superexchange is weaker than the Mn(1)–O–Cr super-exchange, thus effectively resulting in ferrimagnetism. From a simple 3-site Hubbard model, we derived expressions for the antiferromagnetic superexchange strength $J_{AFM}$ and also for the weaker ferromagnetic $J_{FM}$. The relative strengths of $J_{AFM}$ for the various superexchange interactions are in agreement with those obtained from DFT. The expression for Cr–O–O–Cr super-superexchange strength ($\tilde{J}_{SS}$), which has been derived considering a 4-site Hubbard model, predicts a ferromagnetic exchange in agreement with DFT. Finally, our mean field calculations reveal that assuming a set of four magnetic sub-lattices for Mn$^{2+}$ spins and a single magnetic sublattice for Cr$^{3+}$ spins yields a much improved $T_{C}$, while a simple two magnetic sublattice model yields a much higher $T_{C}$.

Keywords: density functional theory, magnetism, wannier functions

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1. Introduction

The perovskite oxide materials are known to exhibit a wide range of properties like complex magnetic structures, multiferroicity, metal–insulator transition and colossal magnetoresistance. Among the basic perovskites (ABO$_3$: A-divalent element, B-transition metal (TM)), the simplest perovskite structure is the cubic structure (space group: Pm3m). Examples are SrTiO$_3$, SrCrO$_3$ and BaTiO$_3$ [1–3], that are cubic at higher temperatures, though they undergo a cubic-tetragonal structural transition. An important parameter, that explains the deviation of the perovskite from simple cubic structure, is the Goldschmidt tolerance factor, defined as, $t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)}$, where $r_A$, $r_B$ and $r_O$ are the ionic radii of the A- and B-site cations and O$^{2-}$ ion, respectively. When ‘t’ becomes less than unity, structural distortions occur, due to which the perovskite compound can crystallize in the tetragonal, rhombohedral or orthorhombic structure [4, 5]. Another type of distortion which occurs in the perovskites (with A-site divalent) is the formation of lone pairs, which results in ferroelectric distortion. An example of this is PbVO$_3$, (space group P4mm), in which off-centering of Pb and V is accompanied by a distortion of the VO$_6$ octahedra [6, 7]. When the A-site consists of a trivalent element (e.g. Sc, Y, or a lanthanide), additional structural distortions occur which include tilting of the BO$_6$ octahedra as well as the Jahn Teller effect [8–10], giving rise to a diverse range of properties [10–14].

Addition of another transition metal atom at B-site in a regular pattern, in the cubic perovskite unit cell, results in doubling of the unit cell. The new compound, A$_2$BB’O$_6$ with the cubic space group Fm3m, is known as the double perovskite [15–17]. Most of the double perovskite compounds have a rock-salt arrangement of the B’/B’’ atoms. Increase in the difference between the size of the A- and B’/B’’-site cations reduces the tolerance factor below unity, thereby resulting in tetragonal (I4/m) [18], (P4$_2$/n) [19], rhombohedral(R3) [20], and the most common monoclinic space group (P2$_1$/n) [21–23] structure. When A is a divalent element, BB’ belong to 3d and 4d/5d groups, respectively, the compounds show ferrimagnetism with a Curie temperature above 300 K, and also a large magnetoresistance [24–27].

When B’ is a non-magnetic p-element (e.g. Sb), the magnetism arises entirely due to the B-sublattice. Due to a greater separation between the B-site atoms, there occurs a drastic reduction in the magnetic transition temperature along with possible occurrence of magnetic frustrations [28]. For instance, Ca$_2$CrSbO$_6$ is a ferromagnet with a $T_C$ of 16 K, while Sr$_2$CrSbO$_6$ is an antiferromagnet with a $T_N$ value of 12 K [29, 30], even though both the compounds crystallize in the monoclinic (P2$_1$/n) structure.

Recently, double perovskites of the form Mn$_2$MSbO$_6$ and Mn$_2$MReO$_6$ ($M$: Sc, Cr, Fe, Co and Mn) [31–33] have been reported experimentally. These compounds also have a monoclinic (P2$_1$/n) structure with the Mn atom at the A-site in the 2+ ionic state and a four-fold oxygen coordination. Combining Mn and Ca results in the solid solution Ca$_{2-x}$Mn$_x$MSbO$_6$ which retains the single phase monoclinic structure for 0 < x < 0.17 and 1.73 < x ≤ 2. For 0.74 < x < 1.1, the compositions crystallize in the tetragonal P4$_2$/n structure while the remaining composition ranges show a two-phase co-existence [34]. We have chosen the composition with x = 1, also known as the double-double perovskite compound, with the general chemical formula AA’BB’O$_6$, as the subject of the present study. These compounds show a dual cationic order, with a columnar arrangement of the A/A’ atoms and a rocksalt arrangement of the B/B’ atoms and with lattice parameters close to those of the cubic Fm3m unit cell [34].

The present work is a DFT based study on a recently synthesized double–double perovskite CaMnCrSbO$_6$ [35], belonging to the Ca$_{2−x}$Mn$_x$CrSbO$_6$ series. The two end compounds of this series, Ca$_2$CrSbO$_6$ and Mn$_2$CrSbO$_6$ have a monoclinic structure (P2$_1$/n), but show entirely different magnetic behaviour. The former shows a long range ferromagnetic order [29] while Mn$_2$CrSbO$_6$ orders antiferromagnetically at $T_N = 55$ K, with a propagation vector $\vec{k} = (0.5,0,0.5)$ [31]. Thus due to Mn$^{2+}$ and Cr$^{3+}$ ions, one could expect that the exchange interactions may lead to a complex long range magnetic structure or spin glass like behaviour in CaMnCrSbO$_6$. However, magnetic neutron diffraction and bulk magnetization studies confirm a collinear ferrimagnetic structure with oppositely aligned Mn$^{2+}$ and Cr$^{3+}$ spins having an ordering temperature, $T_C = 49$ K. The structural neutron diffraction studies also show that due to similar ionic radii, anti-site disorder occurs between the Cr/Mn and Cr/Sb sites, which affects the magnetic properties [35]. Thus, to understand the magnetic structure in the structurally ‘ordered’ unit cell, it is essential to estimate the magnitude and signs of various exchange constants (J) present in the system, which forms an important part of the present work. The origins for these exchange interactions are analyzed in terms of hopping between the different metal-and ligand-Wannier orbitals. Using a simpler formalism of a 3-site Hubbard model with a ground state comprising of single half-filled d-orbital at each transition metal ion site and a doubly occupied O p-orbital, we have estimated the Mn–O–Mn, Mn–O–Cr superexchange interaction strengths. Similarly, the more complex Cr–O–O–Cr super-exchange strength is also estimated from a 4-site Hubbard model with similar ground state as above. In order to determine $T_C$, we consider a model with four Mn$^{3+}$ magnetic sub-lattices and one magnetic sub-lattice for the Cr$^{3+}$ spins. The results thus obtained provide good agreement with the experimental observations and offer a comprehensive picture of the magnetic structure of CaMnCrSbO$_6$.

This paper is organized as follows: after presenting the computational details in section 2, we discuss in section 3, the crystal structure. Section 4.1 comprises of the non-magnetic density of states (DOS) along with the Wannier function analysis. In section 4.2, we discuss the effect of Hubbard U on the electronic and magnetic structures, while in section 4.3 the effects of anti-site disorder on the electronic structure.
and magnetism are discussed. We have shown estimation of the various exchange interactions in section 4.4, while in section 4.5 we discuss the superexchange mechanisms in terms of metal-ligand hopping integrals, with expressions for \( J \) derived using 3-site and 4-site Hubbard model. Finally in section 4.6, we present calculation on estimation of the magnetic transition temperature using the mean field theory.

2. Methodology: computational details

The calculations have been performed using the experimental structural parameters, using DFT as implemented in the Vienna \textit{ab initio} simulation package which uses the projector augmented wave method [36]. The Perdew–Burke–Ernzerhof potential has been employed within the GGA (Generalized Gradient Approximation) and GGA+\( U \) [37, 38]. A cut-off energy of 500\,eV is used in the expansion of the plane waves. A \( 9 \times 9 \times 9 \) Monkhorst–Pack \( k \)-mesh centered at \( \Gamma \) point in the Brillouin zone (BZ) is used for performing the BZ integrations. The electrons from Cr/Mn: 3\( d \), 4\( s \), O: 2\( s \), 2\( p \) and Sb: 4\( f \), 5\( p \), 5\( d \), 6\( s \) and Ca: 3\( p \), 4\( s \) states were considered as the valence electrons. Non-magnetic as well as spin-polarized self-consistent calculations have been performed. Also, non-collinear calculations were also performed within the GGA+\( U \)+\textit{SO} formalism. Further, to obtain the local orbital representation, real-space Wannier functions derived from Mn- and Cr- 3\( d \) orbitals are constructed for the non-magnetic (NM) phase. Disentanglement has been achieved by employing a suitable energy window around the Fermi energy. Based on the band structure, the energy interval between \(-5\) and \(+2\)\,eV was considered for performing the Wannier calculations. For optimal fitting in this energy range and for obtaining the maximally localized Wannier orbitals (MLWFs), we consider all the five \( d \)-orbitals of Mn and Cr, and the three \( p \)-orbitals of O, thus involving 20 Cr, 10 Mn(1), 10 Mn(2) and 72 O-wavefunctions. The calculations are performed on a \( 7 \times 7 \times 7 \) \( k \)-grid. The total spread of Wannier functions was converged upto an order of \( 10^{-10} \) with the total spread of 147.9 \( \text{Å}^2 \). The crystal-field-split onsite energies and hopping amplitudes have also been derived.

3. Crystal structure and local symmetry

The double–double perovskite compound CaMnCrSb\(_{6}\) crystallizes in the tetragonal space group \( P4_{2}nm \). The unit cell (figure 1) comprises of four formula units: 24 O, 4 Mn, 4 Cr, 4 Sb and 4 Ca atoms. The site symmetries of the atoms are as follows: Ca–4\( e \), O–8\( g \), Sb–4\( c \), Cr–4\( c \), Mn(1)–2\( a \) and Mn(2)–2\( b \), respectively. The Mn(1) atoms are coordinated by four oxygen atoms in tetrahedral symmetry (figure 3(a)), while the Mn(2) atoms are coordinated by four oxygen atoms in a square-planar geometry (figure 3(b)). The Cr atoms occupy the 4c-site with a six-fold coordination of oxygen atoms in a highly distorted octahedra, showing both, orthorhombic and GdFeO\(_{3}\)-like distortions (figure 3(c)). In this structural arrangement, the Mn(1), Mn(2) and Cr ions have formal valency of \(+2\), \(+2\) and \(+3\), respectively.

4. Results and discussion

4.1. Non-magnetic electronic structure, Wannier orbitals and on-site energies

The non-magnetic electronic structure calculations yield a metallic state for CaMnCrSb\(_{6}\) as seen from the DOS (figures 2(a)–(c)). The \( d \)-orbitals show significant spectral weight at the Fermi energy (\( E_F \)), in comparison to the O \( p \)-orbitals (not shown). The effect of the crystal-field splittings on the different magnetic ions is seen in the partial DOS. Due to tetrahedral crystal field, the \( d \)-orbitals of Mn(1)\(^{2+}\) ion split into a two-fold degenerate \( E(d_{z^2-r^2}) \) and \( d_{x^2-y^2} \) orbitals which are at lower energy, while the three-fold degenerate \( T(d_{xy}, \, d_{xz} \text{ and } d_{yz}) \) orbitals are at higher energy (figure 3(a)). Figure 2(a),

Figure 1. (a) Crystal structure of CaMnCrSb\(_{6}\). The inequivalent Mn atoms are marked as Mn1 and Mn2.

Figure 2. (a)–(c) Site-resolved non-magnetic partial \( d \)-DOS of CaMnCrSb\(_{6}\). The Fermi energy is at 0\,eV.
shows a clear separation between the E- and T- DOS of the Mn(1) atom with peaks at $\sim -0.5$ and $+0.5$ eV, respectively, in agreement with the local symmetry (figure 3(a)).

The $d$-orbitals of the Mn(2)$^{2+}$ ion, which experience a planar crystal field, split into a set of four levels. The lowest levels which comprise of $d_{xy}/d_{xz}$ orbitals belong to the two-fold degenerate $E_g$ representation. The $d_{yz}$ orbital, belonging now to the $B_{2g}$ representation, lies above the $d_{xy}/d_{xz}$ orbitals (figure 3(b)). The $d_{x^2−y^2}$ and $d_{3z^2−r^2}$ orbitals are non-degenerate and belong to the $B_{1g}$ and $A_{1g}$ representations, respectively. The $d_{x^2−y^2}$ orbital has the highest energy. The $d$-DOS of Mn(2) atom (figure 2(b)) shows features in accordance with the planar geometry. While the $d_{3z^2−r^2}$ DOS shows a large peak at $E_F$, the $d_{x^2−y^2}$ DOS shows a peak at $+1$ eV.

For the Cr$^{3+}$ ion, being at the centre of an orthorhombically distorted octahedron, the $T_{2g}$ ($d_{xz}$, $d_{yz}$ and $d_{xy}$) and $E_g$ ($d_{x^2−y^2}$ and $d_{3z^2−r^2}$) orbitals undergo additional splitting, lifting the degeneracy completely. As shown in figure 3(c), the $T_{2g}$ orbitals of Cr$^{3+}$ split to form a set of three non-degenerate $B_{2g}$ orbitals, while the degenerate $E_g$ orbitals form a linear combination of $d_{x^2−y^2}$ and $d_{3z^2−r^2}$ orbitals resulting in two non-degenerate $A_{1g}$ and $B_{1g}$ orbitals. The $d$-DOS of Cr (figure 2(c)) comprises of partially occupied $d_{xy}$, $d_{xz}$ and $d_{yz}$ states at $E_F$, while the $d_{x^2−y^2}$ and $d_{3z^2−r^2}$ states occur mostly above $E_F$.

In order to estimate the crystal-field splitting in the TM ions, along with the various hopping integrals, the Bloch states obtained in terms of augmented plane wave basis have been expressed in terms of real space Wannier orbitals, considering the $d$-orbitals of both, Mn and Cr along with the $p$-orbitals of oxygen. In figure 3, we show the Wannier orbitals of Mn(1), Mn(2) and Cr atoms.

From the Wannier analysis, we obtain the hopping amplitudes between the TM ion and oxygen atoms. The on-site energies of Mn(1), Mn(2) and Cr $d$-states (listed in table 1), follow the crystal-field splitting scheme as shown in figures 3(a)–(c). The total crystal-field splitting is the smallest for Mn(1), as it is expected for an Mn(1)$^{2+}$ ion placed in a tetrahedral environment, while the Cr$^{3+}$ ion placed in a highly distorted octahedral environment exhibits the maximum splitting. These hopping amplitudes would be utilized later, in the context of superexchange interactions.

### 4.2. Spin polarized electronic structure and effect of correlations

The spin polarized calculations have been carried out for the ferrimagnetic (FiM) configuration, with the Mn$^{2+}$ and Cr$^{3+}$ spins arranged as spin-up and spin-down, respectively. Additionally, the calculations have also been performed for ferromagnetic (FM) and various anti-ferromagnetic (AFM) arrangements, viz. A-type, C-type, and G-type. The calculations, for all the magnetic configurations, have been performed for different values of $U_{\text{e}}(=U−J_H$; $U$ is the Coulomb interaction energy of the $d$-orbitals, $J_H$ is the Hund’s exchange energy). The $U$ value was varied between 0 and 6 eV, with $J_H = 1$ eV for both, Mn and Cr. Calculations were also performed for unequal values of $U$ and $J_H$ in Mn and Cr but with same value of $U_{\text{e}}$. For AFM calculations, either the Mn or the Cr sublattice was fixed in FM configuration, while the other sublattice was arranged as A-type, C-type and G-type. As seen from table 2, at $U_{\text{eff}} = 0$ eV, the FiM configuration has the lowest energy. With the increase in $U_{\text{eff}}$, the difference between the energies of various configurations gets reduced and at $U_{\text{eff}} = 5$ eV, the FiM no longer corresponds to the lowest energy configuration.

In figures 4(a)–(c), we show the spin polarized DOS of CaMnCrSbO$_6$ for the FiM configuration corresponding to $U_{\text{eff}} = 0$ eV. Even in the absence of Hubbard $U$, FiM CaMnCrSbO$_6$ shows an insulating behaviour with a fairly large band gap of $\sim 0.7$ eV. As seen from figures 4(a) and (b), the spin-up $d$-states of Mn(1) and Mn(2) are fully occupied, while spin-down $d$- states are empty. The energy scheme of the crystal field split levels in the NM DOS case (figure 2) is found to be applicable in the FiM configuration as well.

In Mn(2), the $d_{x^2−y^2}$ spin-up DOS occurs in isolation near $E_F$ with a peak at $\sim 0.3$ eV, while the spin-up DOS of the remaining four $d$-states shows sharp peaks between $−1.7$ and $−2.0$ eV. In figure 4(c), the spin-down states of Cr are partially occupied, with the $d_{xz}$ and $d_{yz}$ spin-down DOS showing sharp peaks at $~−0.5$ eV, while the $d_{xy}$ DOS shows a broader feature, with a peak at $−0.2$ eV. The $d_{3z^2−r^2}$ and $d_{x^2−y^2}$ spin-down DOS occur above $E_F$, overlapping with the unoccupied $T_{2g}$ spin-up DOS above $+1.5$ eV.

In figures 4(d)–(f), we show the FiM partial DOS of CaMnCrSbO$_6$ for $U_{\text{eff}} = 3$ eV. The effect of $U$ is different for each atom, though there occurs a broadening, in general. For the Mn(1) atom, the separation between the spin-up $d_{x^2−y^2}$ and $d_{3z^2−r^2}$ DOS shows an increase. The spin-up $d_{xz}/d_{yz}$ states are nearest to $E_F$. For Mn(2) atom, the spin-up $d_{x^2−y^2}$ DOS (figure 4(e)) retains its proximity to $E_F$. For the remaining $d$-states of Mn(2), the DOS is spread in the range $−1.1−5$ eV. The unoccupied Cr spin-down $d_{x^2−y^2}$ and $d_{3z^2−r^2}$ DOS are shifted to $+2$ eV with accentuated peaks, thus resulting in a larger bandgap ($\sim 1.7$ eV) for CaMnCrSbO$_6$ with $U_{\text{eff}} = 3$ eV. In figure 5(a), we show the variation of bandgap in CaMnCrSbO$_6$ as a function of $U_{\text{eff}}$. There occurs a bandgap of $\sim 0.7$ eV for $U_{\text{eff}} = 0$ eV. After a sudden jump, with further increase in $U_{\text{eff}}$, the bandgap shows a gradual increase with correlation energy. Thus CaMnCrSbO$_6$ shows the typical characteristics of a Mott-Hubbard insulator. In figure 5(b), we also show the variation of magnetic moment of Mn and Cr. The variation in

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### Table 1. On-site energies (eV) of the crystal field levels of Mn(1)$^{2+}$, Mn(2)$^{2+}$ and Cr$^{3+}$

|         | $d_{xy}$ | $d_{xz}$ | $d_{yz}$ | $d_{x^2−y^2}$ | $d_{3z^2−r^2}$ | $E_{\text{min}} − E_{\text{max}}$ (eV) |
|---------|---------|---------|---------|--------------|--------------|----------------------------------|
| Mn(1)$^{2+}$ | 6.37    | 6.32    | 6.31    | 6.14         | 6.03         | 0.34                             |
| Mn(2)$^{2+}$ | 6.32    | 6.38    | 6.38    | 6.82         | 6.51         | 0.50                             |
| Cr$^{3+}$   | 6.11    | 6.06    | 6.13    | 6.90         | 6.66         | 0.84                             |
Figure 3. (a)–(c) The local point group symmetries along with corresponding crystal field splitting schemes for (a) Mn(1), (b) Mn(2) and (c) Cr. (a1)–(e1), (a2)–(e2) and (a3)–(e3) correspond to the $d_{3z^2-r^2}$, $d_{xz}$, $d_{yz}$, $d_{xy}$ and $d_{x^2-y^2}$ Wannier $d$-orbitals of Mn(1), Mn(2) and Cr, respectively, in CaMnCrSbO$_6$. The $x$, $y$ and $z$ axes correspond to the $a$, $b$ and $c$ axes of the crystal.

Table 2. Total energy per unit cell (in meV) w.r.t that for the FM configuration for various magnetic configurations and different $U_{\text{eff}} = U - J_H$ (in eV) values. The values of $U$ and $J$ are same for Mn and Cr, unless mentioned otherwise. The lowest energy is highlighted in bold.

| Magnetic Configuration | $U = 0$ | $U = 4$ | $U = 6$(Mn), 5.5(Cr) | $U = 6$ |
|------------------------|---------|---------|---------------------|---------|
| FM                     | 0.0     | 0.0     | 0.0                 | 0.0     |
| FiM                    | -227.0  | -73.4   | -20.8               | -10.8   |
| Cr-A(AFM)              | -62.9   | -6.0    | 13.9                | 17.5    |
| Cr-C(AFM)              | -62.8   | -3.5    | 16.6                | 31.3    |
| Cr-G(AFM)              | -62.8   | -3.5    | 16.6                | 31.3    |
| Mn-A(AFM)              | -127.2  | -53.7   | -16.5               | -15.4   |
| Mn-C(AFM)              | -131.9  | -48.9   | -15.4               | -13.0   |
| Mn-G(AFM)              | -94.5   | -42.5   | -14.1               | -14.1   |
Figure 4. Ferrimagnetic DOS of CaMnCrSbO$_6$ for $U_{\text{eff}} = 0$ eV (left panel) and $U_{\text{eff}} = 3$ eV.

Figure 5. Variation of (a) energy gap and (b) magnetic moments with $U_{\text{eff}}$. Mn(1) and Mn(2) show the same variation on this scale. Moments of Mn(1) and Mn(2) are identical. While Cr attains the fully saturated moment of 3 $\mu_B$ for $U_{\text{eff}} = 3$ eV, Mn(1) and Mn(2) show a slight reduction, from the expected value of 5 $\mu_B$ in their magnetic moments.

4.2.1. Non-collinear calculation and anisotropy. Studies reveal that below the Neel temperature, CaMnCrSbO$_6$ orders magnetically in the $\Gamma_3$ representation [35]. In this, the x- and y-components of the spins within the Mn(1)$^{2+}$ and Mn(2)$^{2+}$ sub-lattices are ferromagnetically coupled, though there is no restriction on the inter-sublattice coupling. The four Cr$^{3+}$ spins in the unit cell are anti-ferromagnetically coupled in the x- and z-directions, and ferromagnetically coupled in the y-direction.

Thus experimentally, it is not resolved, whether the Mn$^{2+}$/Cr$^{3+}$ spins are along the x- or the y-directions; which is decided by the magnetocrystalline anisotropy of the system. Hence to probe the single-ion anisotropy energy, noncollinear calculations have been performed by including the effects of spin–orbit coupling. We have used $U = 6$ eV, $J_H = 1.5$ eV for Mn and $U = 5.5$ eV, $J_H = 1$ eV for Cr. Self consistent calculations were performed for the Mn$^{2+}$ and Cr$^{3+}$ spins aligned along the x-, y- and z-directions. We find that the configuration with the Mn$^{2+}$ and Cr$^{3+}$ spins in the x-direction correspond to the lowest energy (set to 0 meV), while the spins in the y and z-directions yield higher energy by 0.26 and 0.29 meV per unit cell respectively, thus conforming to the experimental results.

4.3. Effect of anti-site disorders

Structural studies in CaMnCrSbO$_6$ reveal up to 20% Mn(Cr) anti-site disorder and 5% Cr(Sb) anti-site disorder [35]. The reduced magnetic moment of 3.8 $\mu_B$, obtained from magnetic neutron diffraction for both Mn$^{2+}$ spins, has been attributed to the ASDs [35]. To probe the effect of ASD on the magnetic and electronic structure of CaMnCrSbO$_6$, we have performed additional spin polarized calculations with inclusion of ASDs. Three independent calculations (in the FiM configuration, with $U_{\text{eff}} = 5$ eV for Mn and Cr): one, where there is no ASD (labelled as ‘Ordered’), other with an exchange between Mn and Cr atoms (labelled as ASD1), and the third where Sb and Cr atoms are exchanged (labelled as ASD2) were carried out. A supercell with lattice parameters $(a, a, 2c)$ containing 8 atoms each of Mn, Cr and Sb was employed for all the three cases. In ASD1, one Cr atom is switched with an Mn atom (we chose Mn(1) site for this), while in ASD2, one Cr atom is switched with an Sb atom. The resulting percentage disorders (12.5% in ASD1 and ASD2, each) within the supercell are fair representatives of those from structural analysis.

We show the total d-orbital DOS of FiM CaMnCrSbO$_6$ with $U_{\text{eff}} = 5$ eV in the regular structure (figure 6(a)) and ASD structures (figures 6(b) and (c)). The DOS of the regular structure is similar to that obtained for $U_{\text{eff}} = 3$ eV, except for a larger band gap now, i.e. ≈2.1 eV. The inclusion of ASD drastically affects the DOS. In ASD1, the spin-up and spin-down DOS of the unswitched Mn and Cr atoms are about 1 eV below
Figure 6. FiM DOS of CaMnCrSbO$_6$ for $U_{\text{eff}} = 5$ eV, in (a) ordered, (b) ASD1 and (c) ASD2 structures.

Table 3. Magnetic moments and band gap in supercells of FiM CaMnCrSbO$_6$ for $U_{\text{eff}} = 5$ eV in ordered and ASD configurations. The prime corresponds to the position after switching of the atoms. The total energy w.r.t. ordered supercell is also mentioned.

| Atom (Position) | Magnetic Moment ($\mu_B$) | Band gap (eV) | Total energy (eV) |
|-----------------|--------------------------|--------------|------------------|
| Ordered         |                          |              |                  |
| Mn(1)(0.25, 0.25, 0.25) | 4.71                  |              |                  |
| Mn(2)(0.75, 0.75, 0.25) | 4.73                  | 2.0          | 0                |
| Cr(0, 0, 0)     | -3.10                   |              |                  |
| Cr(0.5, 0.5, 0) | -3.10                   |              |                  |
| Sb(0, 0, 0.5)  | 0.00                    |              |                  |
| ASD1            |                          |              |                  |
| Mn(2)(0.75, 0.75, 0.25) | 4.71                  |              |                  |
| Mn'(0, 0, 0)    | -3.96                   | 0.1          | +2.18            |
| Cr(0.5, 0.5, 0.0) | -3.10                  |              |                  |
| Cr'(0.25, 0.25, 0.25) | 3.96                  |              |                  |
| Sb(0, 0, 0.5)  | 0.00                    |              |                  |
| ASD2            |                          |              |                  |
| Mn(1)(0.25, 0.25, 0.25) | 4.71                  |              |                  |
| Mn(2)(0.75, 0.75, 0.25) | 4.73                  | 0.7          | +2.31            |
| Cr(0.5, 0.5, 0) | -3.10                   |              |                  |
| Cr'(0, 0, 0.5) | -3.06                   |              |                  |
| Sb'(0, 0, 0)   | 0.00                    |              |                  |

$E_F$, as seen from figure 6(b). The spin-up DOS just below $E_F$ is dominated by the $d$-DOS of the Cr atom, which shows sharp peaks at $\sim -0.2$ and $\sim -0.5$ eV. Similarly, the spin-down DOS just below and above $E_F$ comprises sharp peaks due to $d$-DOS of the Mn atom, thereby making the band-gap almost negligible in ASD1. The ASD2 does not affect the magnetic moments, even though it partially affects the DOS and reduces the band gap. As seen in figure 6(c), in ASD2 structure, the band gap has reduced to $\sim 0.7$ eV, due to the switched Cr $d$-states, which contribute to the spin-down DOS just below $E_F$.

The total $d$-electron occupation number obtained for Mn(1), Mn(2) and Cr in the ordered supercell are 5.06, 5.03 and 4.23 respectively. While in Mn(1) and Mn(2), the $d$-occupation number is quite in agreement with the formal valency of +2 ($3d^6$), the $d$-occupancy of Cr is considerably higher than that expected from a valency of +3 ($3d^3$), thus indicating a greater charge transfer nature. In ASD1, the occupancy of Mn’ has decreased to 4.88, while that of Cr’ has increased to 4.40. The changes in occupation are thus reflected in the magnetic moment of the switched atoms. As seen from table 3, the magnitude of Mn’ magnetic moment has reduced to 3.96 $\mu_B$, while Cr’ shows an enhanced magnetic moment of magnitude 3.96 $\mu_B$. In ASD2, though the occupancy of Cr’ increases to 4.34, a similar increase in Cr’ magnetic moment is not observed. The inclusion of ASDs results in an overall decrease in the magnetic moment of Mn within the supercell, in accordance with the experiments.

4.4. Determination of exchange constants

The stability of the FiM ground state can be understood in a better manner with the help of the various exchange constants in the system. Since CaMnCrSbO$_6$ is found to be insulating from our electronic structure calculations, the exchange interactions are superexchange in nature. The strength of exchange constants decrease with the Hubbard $U$ [39]. Experimental (XPS) and theoretical studies on MnO (an Mn$^{2+}$ system) reveal a high $U$ value of nearly 7 eV is essential to reproduce the various properties [40, 41]. On the other hand, in LaCrO$_3$ (a Cr$^{3+}$ system), a $U = 5.5$ eV successfully reproduces the XPS spectra [40], while the bandgap value is reproduced upon considering $U_{\text{eff}} = 4.5$ eV ($U = 5$ eV, $J_H = 0.5$ eV) [42]. Similar
band structure studies on Ca₃CrSbO₆ (also a Cr³⁺ compound) consider $U_{\text{eff}} \approx 4$ eV ($U = 5$ eV and $J_H = 0.9$ eV) [30].

Thus based on literature, $U_{\text{eff}}$ in the range $4–5$ eV could be considered appropriate for CaMnCrSbO₆. However, since beyond $U_{\text{eff}} = 4.5$ eV, the ferrimagnetic state is no longer the ground state (table 2), we have considered $U_{\text{eff}} = 4.5$ eV for both, Mn as well as Cr with $U = 6(5.5)$ eV and $J_H = 1.5(1)$ eV for Mn(Cr). Though the value of $J_H$ in Mn is higher by atleast 0.5 eV than usually considered, within the Dudarev formalism [43] it is the $U_{\text{eff}}$ that occurs in the calculation for total energy. Moreover, the ratio of $J_H/U = 0.25$ for Mn has been used in various theoretical works on iron based superconductors like pnictides and chalcogenides [44, 45]. The exchange interactions ($J$’s) were evaluated by mapping the total energy of the various magnetic configurations (table 2) to the Ising model Hamiltonian,

$$H = - \sum_{i<j} J_{ij} S_i^z S_j^z$$

(1)

where $J_{ij}$ is the exchange interaction strength, while $S_i^z$ and $S_j^z$ correspond to Mn³⁺ or Cr³⁺ spins, as per applicability. Due to presence of two different transition metals, there occur multiple exchange paths. The various exchange mechanisms can be understood from the magnetic lattice, shown in figure 7. In table 4, we list the various $J$’s in order of increasing distance ‘d’ for different sets of TMs in the magnetic lattice. Considering only the magnetic atoms, we note that Cr atoms are the nearest neighbours to both, Mn(1) and Mn(2) atoms. Each Cr atom has two Mn(1) and two Mn(2) atoms as the nearest neighbours. Due to different ligand environment of the Mn(1) and Mn(2) atoms, we expect the Mn(1)–Cr and Mn(2)–Cr exchange interactions as distinct. The Mn(1) atoms are flanked by two Mn(2) atoms along the c-axis as nearest neighbours and vice versa. In the $a – b$ plane, each Mn(1) is surrounded by four Mn(2) atoms and vice-versa. The Mn(1)–Mn(2) separation in the $a – b$ plane is much larger and is similar as the Cr–Cr separation. For each Cr atom, there are twelve next nearest neighbour Cr atoms, with four Cr atoms in the (110), (101) and (011) planes, each. The corresponding Cr–Cr interactions are denoted as $J_1^{101}$, $J_2^{101}$ and $J_2^{011}$, respectively. Substituting $S_{\text{Mn}} = \pm 5/2$ and $S_{\text{Cr}} = \pm 3/2$ for the Mn²⁺ and Cr³⁺ spins, respectively, the Ising Hamiltonian is expanded for the different magnetic configurations. The total energy in the FM and FiM configurations can be expanded as,

$$E_{\text{FM}} = -25J_1 - 50J_2 - 18J_1^{010} - 18J_2^{010} - 18J_2^{101} - 30J_1^{10} - 30J_1^{01}$$

(2)

$$E_{\text{FiM}} = -25J_1 - 50J_2 - 18J_1^{010} - 18J_2^{010} - 18J_2^{101} + 30J_1^{10} + 30J_1^{01}.$$  

(3)

To obtain Mn(1)–Cr and Mn(2)–Cr exchange constants, i.e. $J_1^{ab}$ and $J_2^{ab}$, unambiguously, two additional calculations were performed. In both the calculations, among the four Cr³⁺ spins in the unit cell, a single Cr³⁺ spin was fixed as spin-down. In the first configuration (denoted as configuration $M$), a single Mn(1)²⁺ spin was kept as spin-down, and in the second case (denoted as configuration $N$), a single Mn(2)²⁺ spin was fixed as spin-down. Due to cancellation of most of the terms, the total energy for configurations $M$ and $N$ reduces to,

$$E_{M} = -15J_1^{10}$$

$$E_{N} = -15J_1^{01}. \tag{4}$$

Our calculations show that the energies of both the configurations $M$ and $N$ are higher than that of FM by +8.33 and +4.93 meV per unit cell, respectively. From equations (2)–(4), we obtain $J_1^{10} = -0.41$ meV and $J_1^{01} = -0.06$ meV. The negative values indicate that these exchange interactions are antiferromagnetic in nature. The differences in the local environment of both the Mn²⁺ ions result in a large difference between Mn(1)–Cr and Mn(2)–Cr interaction strengths. To obtain the exchange interactions within the individual Mn and Cr sublattices, we refer to the calculations in which (a) Mn sublattice was kept fixed in FM configuration and magnetic configuration of the Cr sublattice was varied, and (b) Cr sublattice was kept fixed in FM configuration, while the magnetic configuration of the Mn sublattice was varied (table 2). The set of equations for the A-, C- and G-type arrangement of the Mn-sublattice is,

$$E_{\text{Mn}}^{A} = 25J_1 - 50J_2 - 18J_1^{101} - 18J_2^{101} - 18J_2^{011}.$$  

(5)

$$E_{\text{Mn}}^{C} = -25J_1 - 50J_2 - 18J_1^{010} - 18J_2^{010} - 18J_2^{101}, \tag{6}$$

$$E_{\text{Mn}}^{G} = 25J_1 + 50J_2 - 18J_1^{101} - 18J_2^{101} - 18J_2^{011}. \tag{7}$$

Similarly, the set of equations for A-, C- and G-type arrangement of the Cr-sublattice is,

$$E_{\text{Cr}}^{A} = 25J_1 - 50J_2 + 18J_1^{010} + 18J_2^{010} + 18J_2^{101}.$$  

(8)

$$E_{\text{Cr}}^{C} = -25J_1 - 50J_2 + 18J_1^{101} - 18J_2^{101} + 18J_2^{011}, \tag{9}$$

$$E_{\text{Cr}}^{G} = 25J_1 + 50J_2 + 18J_1^{101} + 18J_2^{101} - 18J_2^{011}. \tag{10}$$

After solving the equations (2)–(10), it is found that all the Mn(1)–Mn(2) interactions are anti-ferromagnetic and smaller as compared to the Cr–Cr interactions which are found to
be ferromagnetic. 

For the Cr–Cr interactions, we consider the average of $J_2^{101'}$, $J_2^{011'}$ and $J_2^{101}$ and denote it as $J_2$ since the three values are similar. Despite of having nearly the same separation distance, the Cr–Cr interaction strength in our system is much greater than Cr–Cr exchange strength of $+0.05$ eV, obtained in Ca$_2$CrSbO$_6$ [30]. In table 4 we list all these exchange constants in the column under Method I.

To ascertain the values of $J$’s obtained above, we have independently obtained the exchange parameters, using two additional methods, labelled as Method II and III. In Method II, one magnetic element is entirely replaced by a non-magnetic element. Hence, to obtain the Cr–Cr and Mn–Mn exchange interactions, we carried out calculations in which the Mn(Cr) atoms are replaced by isovalent Zn(Sc) atoms. However, in this method, the inter-sublattice i.e. Mn–Cr exchange interaction strength cannot be determined. The intra-sublattice exchange interactions thus obtained are shown in table 4 in the column Method II. In Method III, except for the two magnetic atoms whose exchange interaction strength is to be determined, rest of the magnetic atoms are replaced by the isovalent non-magnetic equivalents [46]. The corresponding exchange interaction strength is then proportional to the energy difference between the FM and AFM arrangement of the two spins and are listed in table 4 under Method III. The sign of $J$ for the various exchange interactions, obtained from the three methods are consistent, and the magnitudes almost equal, though differences upto 90 meV are found in the case of Cr–Cr interactions. It is noted that these values of nearest neighbour $J$ from DFT studies for this double-double perovskite are an order of magnitude smaller than those found in single and double perovskite compounds for similar values of $U$ and $J_H$ [46–48]. The anti-ferromagnetic nature of Mn(1)–Mn(2) interactions from this work appears contrary to the experimental studies. The ferrimagnetic behaviour obtained from the bulk magnetization and neutron diffraction [35] suggests a parallel alignment of Mn$^{2+}$ spins which is possible only when the Mn(1)–Mn(2) exchange interaction is ferromagnetic. To understand the origin and the sign of the various exchange interactions, we have investigated the superexchange mechanisms in the following section.

4.5. Superexchange from hopping integrals

The exchange interaction strengths obtained in the preceding section can be understood in terms of the hopping amplitudes, between the Wannier orbitals of Mn(1), Mn(2) and Cr via the O $p$-orbitals. The $J$’s have been calculated from the overlap integrals between the metal and the ligand Wannier functions. As shown in figure 3, due to the differences of the point group symmetry and the local coordinate axes of Mn$^{2+}$, Mn$^{2+}$ and Cr$^{3+}$ ions, the nearest neighbour $d$–$p$ hoppings show $\sigma$- as well as $\pi$- character.

In figures 8(a)–(e), we show the magnitudes of the $d$–$p$ hopping integrals ($t_{dp}$), which give rise to the superexchange interaction between the nearest neighbour Mn(1)–Mn(2), Mn(1)–Cr and Mn(2)–Cr spin pairs, while figures 8(i) and (j) correspond to $d$–$p$ hopping associated with the in-plane Mn(1)–Mn(2) superexchange interactions. Figures 8(f)–(h) corresponds to the Cr-Cr exchange occurring via two intermediate $O^{2-}$ ions, and is labelled as ‘super-superexchange’. Thus, while figures 8(f) and (h) correspond to the hopping between the adjacent Cr-O pairs, figure 8(g) represents the hopping between the two $O^{2-}$ ions, denoted by $t_{pp}$. The coordinates of the TM and the intermediate oxygen atoms are also mentioned in the sub-plots. The labels (1a), (2a),… have been placed only for the purpose of identification of the various O atoms. Based on these amplitudes of the $d$–$p$ hoppings, we illustrate some of the possible paths for the nearest neighbour Mn(1)–O(1a)–Mn(2), Mn(1)–O(1a)–Cr, Mn(2)–O(2a)–Cr superexchange interactions in figures 9(a)–(e). The Mn(1)–O(1)–Mn(2) has a bond-angle of $\sim 100^\circ$, while the Mn(1)–O–Cr and Mn(2)–O–Cr bond angles are $\sim 105^\circ$; these can thus be understood in the formalism of the 90$^\circ$ superexchange according to the Goodenough–Kanamori rules [49]. With the $\sigma$- as well as $\pi$- hopping contributing to the superexchange process, the 90$^\circ$ superexchange is more complex, though weaker than the $\sim 180^\circ$ anti-ferromagnetic superexchange which is seen in the perovskite systems [49].

According to basic mechanism of superexchange proposed by Anderson [50], when the hopping between two half filled $d$-orbitals occurs via the doubly occupied $p$-orbital of an intermediate $O^{2-}$ ion, the resultant superexchange interaction is antiferromagnetic. On the other hand, when the virtual electron transfer is from a half-filled to an empty orbital or from a filled to a half-filled orbital, the resultant interaction is ferromagnetic [49]. While in similar double–double perovskite systems CaMnNiReO$_6$ and CaMnCoReO$_6$, due to the itinerant character of the Re-5d electron, a double exchange mechanism is proposed [51], in CaMnCrSbO$_6$ the exchange interactions are superexchange in nature. In this context, we consider a simple 3-site Hubbard model with a single half filled

| Path                  | Method I (meV) | Method II (meV) | Method III (meV) |
|-----------------------|---------------|-----------------|------------------|
| $J'_{1a}$ Mn(1)-Cr    | 3.3031        | −0.41           | −0.46            |
| $J'_{1b}$ Mn(2)-Cr    | 3.3031        | −0.06           | −0.14            |
| $J_1$ Mn(1)-Mn(2)(c-axis) | 3.8104 | −0.07           | −0.11            |
| $J_2$ Mn(1)-Mn(2)(a − b) | 5.3966 | −0.03           | −0.05            |
| $J'_2$ Cr-Cr          | 5.3966        | +0.32           | +0.37            |
Oxygen atoms are mentioned for each panel. \(\text{Mn(2)}-\text{O}-\text{Cr},(f)-(h)\ \text{Cr}-\text{O}-\text{O}-\text{Cr} \) ‘super-superexchange’ \((i)-(j)\ \text{Mn(1)}-\text{O}-\text{Mn(2)}\) (appendix J). The maximum value for the \(\text{Mn(1)}-\text{O}-\text{Mn(2)}\) superexchange, along the \(c\)-direction. The \(J_{\text{AFM}}\) calculated for a few combinations of \(\text{Mn(1)}, \text{Mn(2)}-d\) and \(\text{O}(1a)\) \(p\)-orbitals are listed in figure 10(c).

The superexchange interaction between \(\text{Mn(1)}\) and \(\text{Mn(2)}\) atoms, situated in-plane, occurs through the intermediate \(\text{O}(2b)\) atom. As seen from figures 8(i) and (j), the \(\text{Mn(1)}-\text{O}(2b)\) hopping amplitude is smaller than that for \(\text{Mn(2)}-\text{O}(2b)\). The \(J_{\text{AFM}}\) values for various possible \(\text{Mn(1)}-\text{O}-\text{Mn(2)}\) in-plane superexchange paths are shown in figure 10(d). The highest value of \(J_{\text{AFM}} = -0.12\) meV is obtained for the \(\text{Mn(1)}d_{z^2}-\text{O}(2b)p_y-\text{Mn(2)}d_{z^2}-\text{superexchange}\).

The \(\text{Mn(1)}\)-Cr and \(\text{Mn(2)}\)-Cr exchange can be understood through the superexchange via the \(\text{O}(1a)\) and \(\text{O}(2a)\) \(p\)-orbitals, respectively. In the octahedrally split \(d\)-state of \(\text{Cr}^{3+}\) ion, the \(E_g\) orbitals are unoccupied. However, for comparison, we also consider the various superexchange paths due to \(T_{2g}\) as well as \(E_g\) orbitals of Cr. Thus for the \(\text{Mn(1)}\)-Cr, the highest \(J_{\text{AFM}} (-7.07\) meV) is obtained for the path \(\text{Mn(1)}d_{z^2}-\text{O}(1a)p_x-\text{Cr}^{3+}\). Due to \(\sigma\)-bond, between \(\text{Cr}d_{z^2}-\text{O}(1a)p_x\), the hopping amplitude is the maximum (figure 8(c)), thus the \(\text{Mn(1)}d_{z^2}-\text{O}(1a)p_x-\text{Cr}d_{z^2} \) superexchange path (figure 9(b)), also yields a large value of \(J_{\text{AFM}} (-4.2\) meV). The maximum \(J_{\text{AFM}}\) values (figure 10(a)) considering independent \(d\)-orbitals are an order of magnitude higher than the exchange strength \((J'_{\text{ex}})\) directly obtained from DFT (table 4).

In the case of \(\text{Mn(2)}-\text{O}(2a)-\text{Cr}\) superexchange, the \(\text{Mn(2)}-\text{O}(2a)\) hopping amplitudes are smaller, as compared to those for \(\text{Cr}-\text{O}(2a)\), as shown in figures 8(e) and (d), respectively. In figure 10(b), we show \(J_{\text{AFM}}\) for some of the possible AFM superexchange interaction strengths for \(\text{Mn(2)}-\text{O}-\text{Cr}d_{z^2} - \text{O}(2a)\).
A maximum $J_{AFM}(-3.3 \text{ meV})$ is obtained for the path Mn(2)$d_{x^2-y^2}$–O(2a)$p_y$–Cr$d_{xy}$. In figure 9(c) we show the path Mn(2)$d_{x^2-y^2}$–O(2a)$p_y$–Cr$d_{2x^2-r^2}$, which yields $J_{AFM}=-2.5 \text{ meV}$. The maximum $J_{AFM}$ for Mn(2)–O(2a)–Cr is half of the maximum $J_{AFM}$ obtained for Mn(1)–O(1a)–Cr (figure 10(a)), in agreement with the trend obtained from our DFT calculations.

In a 90° superexchange as is present in our system, ferromagnetic superexchange between the TM ions also occurs due to hopping via two different (orthogonal) $p$-orbitals of the single O$^2-$ ion [49, 52]. Considering the additional $p$-orbital and an exchange coupling ($J_p$) between the two $O$ $p$-orbitals, the exchange interaction strength (appendix B) is,

$$J_{FM} = \frac{\langle \hat{\sigma}_a \hat{\tau}_a \rangle}{U-J_p} + \frac{\langle \hat{\sigma}_b \hat{\tau}_a \rangle}{J_p-U^2} \left( \frac{\hat{\sigma}_a \hat{\tau}_a}{U-J_p} \right) \right) ^2 \left( \frac{\hat{\sigma}_b \hat{\tau}_a}{J_p-U^2} \right) \right) \right) \right). \quad (12)$$

It is worth mentioning here that the $J$'s are obtained by downfolding of the various Hamiltonian matrices into effective Hamiltonian form (appendices A–C) which involve smaller 2×2 matrices. Thus the $J_{FM}$ in equation (12) is obtained in matrix form. Considering the non-zero eigenvalue, $J_{FM}$ is finally obtained as a number. Based on the above formula, the ferromagnetic superexchange strength for Mn(1)$d_{xy}$ and Cr$d_{2x^2-r^2}$ occurring via O(1a)$p_y$ and $p_z$ orbitals (figure 9(d)) yields, $J_{FM}=0.5 \text{ meV}$ (figure 10(a)), an order of magnitude smaller than the largest $J_{AFM}$. The Mn(2)$d_{x^2-y^2}$–O(2a)$p_y$–O(2a)$p_y$–Cr$d_{2x^2-r^2}$ superexchange (figure 9(e)) also yields $J_{FM}=0.5 \text{ meV}$ (figure 10(b)). For the out-of-plane Mn(1)–O–Mn(2) superexchange, the Mn(1)$d_{xy}$–O(1a)$p_y$–O(1a)$p_y$–Mn(2)$d_{xy}$ ferromagnetic superexchange (figure 10(c)) yields $J_{FM}=0.1 \text{ meV}$. Though $J_{FM}$ is always smaller than $J_{AFM}$, this can cause a net decrease in the overall strength of the antiferromagnetic interactions present in our system.

Finally, we discuss the ‘super-superexchange’ between two Cr$^{3+}$ ions, which because of greater distance is in-principle weaker than the rest of the interactions. Due to the identical orthorhombic ligand symmetry, the Cr(0,0,0)–O(1b) hopping is almost identical to the Cr(0.5,0.5,0)–O(3a) hopping (figures 8(f) and (h)). As shown in figure 8(g), maximum hopping occurs between the $p_z$ orbitals of O(1a) and O(3b), thus acting as a bridge for the ‘super-superexchange’ process. Using sixth order perturbation theory, Toyoda et al [53, 54] have calculated the exchange constant for the super-superexchange process ($J_{SS}=-r^2d_{x^2-y^2}\Delta^{-1}t(\Delta^{-1}+U^{-1})$). Considering only a single path Cr$d_{xy}$–O(1b)$p_y$–O(3a)$p_y$–Cr$d_{xy}$ (figure 9(f)) which has maximum hopping amplitudes throughout, we obtain $J_{SS}=-0.25 \text{ meV}$. Though this formula predicts a correct order of magnitude, however, the sign of $J_{SS}$ is anti-ferromagnetic. This discrepancy is due to the fact that the expression is obtained from the assumption that the ground state is made up of empty ligand orbital and a single hole at each TM ion site. This being appropriate for the cuprate superconductors Cu$^{3+}(d^9)$ or Cr$^{3+}(d^4)$ systems, but...
not suitable for our system [55]. Hence, similar to the case of first order superexchange, we extended the formalism to include the second $O^{2-}$ ion and obtained expression for the ‘super-superexchange’ constant $\tilde{J}_{SS}$ (appendix C) as,

$$
\tilde{J}_{SS} = \frac{2t_{pd}^2 (t_{pd}^2 + t_{pp}^2)}{U(U + t_{pd}^2)} - \frac{2r_{pd}^4 t_{pp}^2}{U^3} - \frac{2r_{pd}^4 t_{pp}^2}{U^5} + \frac{4r_{pd}^4 t_{pp}^2}{U^7},
$$

(13)

Using equation (13), we obtain $\tilde{J}_{SS} = 0.075$ meV for $\text{Cr}_{d_{xy}} - \text{O}(1b)p_x - \text{O}(3a)p_x - \text{Cr}_{d_{xy}}$ path, which though smaller has the ferromagnetic character. However, on neglecting $t_{pd}$ in comparison to $U$ in the first term, we obtain a higher value of $\tilde{J}_{SS} = 0.32$ meV, which is close to the value obtained from DFT and hence can be considered as an upper limit. The maximum $\tilde{J}_{SS}$ and $J_{SS}$ are shown in figure 10(c).

4.6. Determination of Curie temperature from mean field theory

Finally, based on the $J$-values obtained from our DFT calculations, we have determined the Curie temperature of CaMnCrSbO$_6$ using mean field theory. Similar to section 4.4, we describe the Mn/Cr sublattices as a system of Ising spins, which is an approximation of the full Heisenberg Hamiltonian. Due to the anti-ferromagnetic Mn(1)-Mn(2) interactions within the $a-b$ plane and $c$-directions, a two-sublattice system followed by Gauvin-Ndiay et al [48] for
double perovskites does not seem valid for the double-double perovskite CaMnCrSbO₆, a relatively more complex system. Hence, we need to regard each Mn²⁺ spin in a unit cell as belonging to a different sublattice. Thus, there are four Mn⁴⁺/⁴⁻ sublattices and one Cr³⁺ sublattice in the crystal. We consider the entire spin lattice to be consisting of 2N spins, with N Cr³⁺ spins and N/4 spins in each magnetic sublattice of Mn²⁺ spins. We denote the z-components of the four different Mn²⁺ sublattice spins and the Cr³⁺ spins as S_m⁰, S_m⁺, S_m⁻, S_m² and S_c, respectively. It may be noted that S_m² and S_m⁻ correspond to Mn(1) atoms, while S_m⁺ and S_m⁰ correspond to Mn(2) atoms. Using the same notation of J’s as in table 4 and figure 7, the exchange Hamiltonian of the equation (1) is now written as,

\[
H = -J_1 \sum_{i,j=1}^{N/4} S_{mi}S_{mj} - J_2 \sum_{i,j=1}^{N/4} S_{mi}S_{mj} - J_1' \sum_{i=1}^{N/4} S_z (S_{mj} + S_{mj}) - J_2' \sum_{i=1}^{N/4} S_z (S_{mi} + S_{mi})
\]

where the exchange (mean) field acting on each sublattice is,

\[
h_{M1} = -\frac{1}{g\mu_B N} (2J_1M_2 + 4J_2M_2 + J_1''M_C)
\]

\[
h_{M2} = -\frac{1}{g\mu_B N} (2J_1M_1 + 4J_2M_4 + J_1''M_C)
\]

\[
h_{M3} = -\frac{1}{g\mu_B N} (2J_1M_4 + 4J_2M_1 + J_1''M_C)
\]

\[
h_{M4} = -\frac{1}{g\mu_B N} (2J_1M_3 + 4J_2M_2 + J_1''M_C)
\]

\[
h_C = -\frac{1}{g\mu_B} (J_1''(M_1 + M_4) + J_1''(M_2 + M_3) + 24J_2'M_C).
\]

In equation (17), N' = N/4. The total Hamiltonian, which comprises of the Zeeman and mean field terms is,

\[
H_{total} = -g\mu_B \left( H_0 + h_{M1} \right) \sum S_{mi} - g\mu_B \left( H_0 + h_{M2} \right) \sum S_{mi}
\]

\[
- g\mu_B \left( H_0 + h_{M3} \right) \sum S_{mi} - g\mu_B \left( H_0 + h_{M4} \right) \sum S_{mi}
\]

\[
- g\mu_B \left( H_0 + h_{C} \right) \sum S_{ci}
\]

In terms of effective mean fields (h_M or h_C) acting on each sub-lattice atom,

\[
H_{MF} = h_M \sum S_{m1} + h_M \sum S_{m2} + h_M \sum S_{m3} + h_M \sum S_{m4}
\]

\[
+ h_M \sum S_{m5} + h_M \sum S_{m6} + h_M \sum S_{m7} + h_M \sum S_{m8}
\]

\[
- M_C \frac{1}{g\mu_B N} \left( J_1'' \sum S_{m1} + J_1'' \sum S_{m2} \right)
\]

\[
+ J_1'' \left( \sum S_{m3} + \sum S_{m4} \right) / g\mu_B N \sum S_{ci}.
\]

\[
15
\]

In terms of effective mean fields (h_M or h_C) acting on each sub-lattice atom,

\[
H_{MF} = h_M \sum S_{m1} + h_M \sum S_{m2} + h_M \sum S_{m3} + h_M \sum S_{m4}
\]

\[
+ h_M \sum S_{m5} + h_M \sum S_{m6} + h_M \sum S_{m7} + h_M \sum S_{m8}
\]

\[
- M_C \frac{1}{g\mu_B N} \left( J_1'' \sum S_{m1} + J_1'' \sum S_{m2} \right)
\]

\[
+ J_1'' \left( \sum S_{m3} + \sum S_{m4} \right) / g\mu_B N \sum S_{ci}.
\]

\[
16
\]

\[
M_{kB} = gS_M \mu_B N' B_s \left( \frac{gS_M \mu_B h_{eff}}{k_B T} \right) (k = 1, \ldots, 4)
\]

\[
M_C = gS_C \mu_B N B_s \left( \frac{gS_C \mu_B h_{eff}}{k_B T} \right)
\]

where B_s(x) = \frac{2\pi}{\pi x} \coth(\frac{\pi x}{\pi}) - \frac{1}{\pi x} \coth(\frac{\pi}{x}) is the Brillouin function. For x << 1, i.e. when g\mu_B h_{eff} << k_B T (a: M or C) which is true for large temperatures, the sub-lattice magnetization for Mn²⁺ and Cr³⁺ spins can be written as,

\[
M_k = g^2 \mu_B^2 N' S_M (S_M + 1) \frac{h_{eff}}{3k_B T}
\]

\[
M_C = g^2 \mu_B^2 N C (S_C + 1) \frac{h_{eff}}{3k_B T}
\]

\[
13
\]
Setting $H_0 = 0$, from equations (18)–(20), we obtain a system of linear equations,

\[
\begin{align*}
M_1 &= \frac{S_M(S_M + 1)}{3k_B T} \left( 2J_1 M_2 + 4J_2 M_3 + J_{\text{eff}} M_C \right) \\
M_2 &= \frac{S_M(S_M + 1)}{3k_B T} \left( 2J_1 M_1 + 4J_2 M_4 + J_{\text{eff}} M_C \right) \\
M_3 &= \frac{S_M(S_M + 1)}{3k_B T} \left( 2J_1 M_4 + 4J_2 M_1 + J_{\text{eff}} M_C \right) \\
M_4 &= \frac{S_M(S_M + 1)}{3k_B T} \left( 2J_1 M_3 + 4J_2 M_2 + J_{\text{eff}} M_C \right) \\
M_C &= \frac{S_C(S_C + 1)}{3k_B T} \left( J_{\text{IA}}(M_1 + M_4) + J_{\text{IB}}(M_2 + M_3) + 24J_5 M_C \right).
\end{align*}
\]

The transition temperature $T_C$ is obtained from the homogenous solution of equation (21) i.e.

\[
\begin{pmatrix}
1 & -2J_1 \tilde{S}_1 / y & -4J_2 \tilde{S}_1 / y & 0 & -J_{\text{eff}} \tilde{S}_C / y \\
-2J_1 \tilde{S}_1 / y & 1 & 0 & -4J_2 \tilde{S}_1 / y & -J_{\text{eff}} \tilde{S}_C / y \\
-4J_2 \tilde{S}_1 / y & 0 & 1 & -2J_1 \tilde{S}_1 / y & -J_{\text{eff}} \tilde{S}_C / y \\
0 & -4J_2 \tilde{S}_1 / y & -2J_1 \tilde{S}_1 / y & 1 & -J_{\text{eff}} \tilde{S}_C / y \\
-J_{\text{eff}} \tilde{S}_C / y & -J_{\text{eff}} \tilde{S}_C / y & -J_{\text{eff}} \tilde{S}_C / y & -J_{\text{eff}} \tilde{S}_C / y & 1 - 24J_5 / y
\end{pmatrix} = 0
\]

where, $y = 3k_B T_C$, $\tilde{S}_1 = S_M(S_M + 1)$, $\tilde{S}_2 = S_C(S_C + 1)$. Solving equation (22), we obtain $T_C = 99$ K, which is closer to the experimental value of 49 K, while the two sublattice model yields a considerably higher value of $\sim 188$ K.

4.7 Conclusion

We have investigated thoroughly the electronic and magnetic structure along with magnetic exchange interactions in the recently reported double-double perovskite CaMnCr$_2$O$_6$. Amongst the various arrangements of Mn$^{2+}$ and Cr$^{3+}$ spins, the lowest energy corresponds to ferrimagnetic configuration, in agreement with the experimental observation. For $U_{\text{eff}} = 0$ eV, a band gap of $\sim 0.7$ eV is obtained which increases on increasing $U_{\text{eff}}$, thereby suggesting that the system has a Mott–Hubbard like character. Our non-collinear calculations reveal that the combined Mn$^{2+}$/Cr$^{3+}$ spins show anisotropy in the crystallographic x-direction, thus resolving the antisymmetry (in the experimental results) about the preferred direction of the spins. The inclusion of the anti-site disorder explains the reduced value of the Mn$^{2+}$ magnetic moments in this compound.

The nearest neighbour (along c-direction) Mn(1)–O–Mn(2) superexchange interactions are antiferromagnetic and weaker than the ferromagnetic Cr–O–O–Cr super-superexchange interactions, while the in-plane Mn(1)–O–Mn(2) superexchange is the weakest in the lattice. The Mn–O–Cr interactions are also predominantly antiferromagnetic. Due to difference in the ligand symmetry between Mn(1) and Mn(2), the Mn(1)–O–Cr superexchange interaction is stronger than the Mn(2)–O–Cr interaction, thereby establishing a ‘ferrimagnetic’ order.

The formula for $J_{\text{AFM}}$ obtained from a 3-site Hubbard model, predicts correct relative strengths for the various anti-ferromagnetic interactions. While the maximum $J_{\text{AFM}}$ for Mn(1)–O–Mn(2) (out of plane and in-plane) is closer to the DFT results, the maximum $J_{\text{AFM}}$ for Mn–O–Cr superexchange is overestimated by an order of magnitude. Using a 4-site Hubbard model, we obtain an expression for the Cr–O–O–Cr super-superexchange $J_{SS}$, which is found to be ferromagnetic, with an upper estimate value in reasonable agreement with the DFT results. We show that considering a set of five magnetic sub-lattices, using the mean field theory one gets a Curie temperature of 99 K, which is closer to the experimental value of 49 K unlike the two-sublattice model which yields a higher Curie temperature.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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Appendix A. AFM Super-exchange interaction

The Hubbard Hamiltonian for the first order nearest neighbour superexchange between two TM ions and a single oxygen ion can be written as [52],

\[
H = - \sum_{\sigma = \uparrow, \downarrow} \epsilon_d \hat{n}_{1\sigma} + \epsilon_d \hat{n}_{2\sigma} + \epsilon_p \hat{n}_{p\sigma} \\
- \sum_{i=1,2} t_{pd} (d_{i\sigma}^+ c_{p\sigma} + c_{p\sigma}^+ d_{i\sigma}) + U_{1\sigma} \hat{n}_{1\sigma} + U_{2\sigma} \hat{n}_{2\sigma}
\]

where, $(d_{i\sigma}^+, d_{i\sigma})$ correspond to the creation and annihilation of the electron in the two d-orbitals, while $(c_{p\sigma}^+, c_{p\sigma})$ correspond the creation and annihilation of the electron at the O p-orbital, and ‘$\sigma$’ corresponds to the two spin states and $\hat{n}_{\sigma} = d_{i\sigma}^+ d_{i\sigma}$ along with $\hat{n}_{p\sigma} = c_{p\sigma}^+ c_{p\sigma}$ are the number operators for the electron in the d- and p-orbital, respectively. $\epsilon_{di}$ $(i=1,2)$ are on-site energies of the d-orbitals of the two TM ions, $\epsilon_p$ is the on-site energy of the p-orbital, $t_{pd}$ is the hopping integral between the TM d- and O p-orbitals, $U_1$ and $U_2$ are Hubbard parameters for the first and second TM ion respectively. Due to the distinct TM ions, (Mn(1)$^{2+}$, Mn(2)$^{2+}$ and Cr$^{3+}$), the various parameters (on-site, hopping and Hubbard) are different, hence we have used additional index ‘i’. The ground state comprises of singly occupied d-orbitals (parallel or anti-parallel). For the Hamiltonian (A1), in the ferrimagnetic case, when both the d-
electron spins point upwards (spin-triplet), the state is denoted by $d^+_p c^+_p |0\rangle$, where $|0\rangle$ denotes vacuum state without any electrons. The matrix representation for the FM is

$$H_{FM} = \begin{bmatrix} 0 & t_{pd1} & t_{pd2} & \tilde{U}_1 & 0 & \tilde{U}_2 & 0 \\ t_{pd1} & 0 & 0 & 0 & 0 & 0 & 0 \\ t_{pd2} & 0 & 0 & 0 & 0 & 0 & 0 \\ \tilde{U}_1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ \tilde{U}_2 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} 0 \rangle \text{(A2)}$$

On the right side of each row of the matrix, we have mentioned the corresponding state in the Hilbert space. The first term of the matrix which corresponds to $\epsilon_{d1} + \epsilon_{d2} + 2\epsilon_p$ is the sum of on-site energies, which is set to be 0. We define, $\Delta_{pd} = \epsilon_{d1} - \epsilon_{d2}$ (i=1,2) as the charge transfer energies. In the above matrix, we have made the following abbreviations, $\tilde{U}_1 = U_1 + \Delta_{pd1}$, $\tilde{U}_2 = U_2 + \Delta_{pd2}$.

Similarly for the AFM (spin singlet) case, when the ground state has a spin-up and spin-down electron, the matrix representation along with the corresponding basis is,

$$H_{AFM} = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} 0 \rangle \text{(A3)}$$

where, $\tilde{U} = \tilde{U}_1 + \tilde{U}_2$ and $\Delta \epsilon = \epsilon_{d1} - \epsilon_{d2}$. The Hamiltonian matrix for the ferromagnetic and antiferromagnetic ground states are written in the block diagonal form. The FM Hamiltonian (A2) can be written as a $2 \times 2$ block matrix,

$$H_{FM} = \begin{bmatrix} H_{00} & T_{01} \\ T_{01} & H_{11} \end{bmatrix} H_{00} = 0, \quad H_{11} = \begin{bmatrix} \tilde{U}_1 & 0 \\ 0 & \tilde{U}_2 \end{bmatrix}, \quad T_{01} = \begin{bmatrix} t_{pd1} \\ t_{pd2} \end{bmatrix} = T_{01}^+ \text{(A4)}$$

In (A4), $H_{11}$ is the diagonal block while $T_{01}$ is the off-diagonal block of (A2). In a similar manner, writing (A3) in block form,

$$H_{AFM} = \begin{bmatrix} H_{00} & T_{01} \\ T_{01} & H_{11} \end{bmatrix} H_{00} = 0, \quad H_{11} = \begin{bmatrix} \tilde{U}_1 & 0 & 0 & 0 \\ 0 & \tilde{U}_2 & 0 & 0 \\ 0 & 0 & \tilde{U}_1 & 0 \\ 0 & 0 & 0 & \tilde{U}_2 \end{bmatrix}, \quad T_{01} = \begin{bmatrix} t_{pd1} \\ t_{pd2} \end{bmatrix} = T_{01}^+ \text{(A5)}$$

In (A5), $H_{00}$ is a $2 \times 2$ null-matrix, $H_{11}$ and $H_{22}$ are the diagonal blocks from (A3). From (A3), the off-diagonal block matrices are,

$$T_{01} = \begin{bmatrix} t_{pd1} \\ t_{pd2} \end{bmatrix} = T_{01}^+, \quad T_{12} = \begin{bmatrix} -t_{pd2} \\ 0 \\ 0 \end{bmatrix}$$

Similarly, substituting the matrices defined in (A5) and (A6) in (A7) we obtain the effective Hamiltonian for the singlet,

$$H_{eff} = -T_{01}H_{11}^{-1}T_{10} = T_{01}H_{11}^{-1}T_{12}H_{22}^{-1}T_{21}H_{11}^{-1}T_{10} \text{(A7)}$$

In the FM case, only the first term exists in (A7), while for the AFM block Hamiltonian both terms in the right hand side of (A7) contribute to $H_{eff}$. Performing the multiplication of various block matrices in (A4) as per (A7) we obtain,

$$H_{eff} = \frac{t_{pd1}^2}{\tilde{U}_1} \frac{t_{pd2}^2}{\tilde{U}_2} \text{(A8)}$$

$$H_{eff} = \begin{bmatrix} \tilde{U}_1 - \frac{t_{pd2}}{\tilde{U}_2} & 0 & -t_{pd2} \\ 0 & \tilde{U}_1 & -t_{pd1} \end{bmatrix} \begin{bmatrix} 1 \\ 0 \\ -t_{pd1} \end{bmatrix}^2$$

$$\times \begin{bmatrix} 1 & 0 \\ \tilde{U}_1^2 & \tilde{U}_2^2 \\ \tilde{U}_1 & \tilde{U}_2 \end{bmatrix} + \begin{bmatrix} 0 \\ 1 \\ 1 \end{bmatrix} \left( \begin{bmatrix} 1 \\ \tilde{U}_1 \end{bmatrix} \times \begin{bmatrix} 1 & 0 \\ \tilde{U}_1 & \tilde{U}_2 \end{bmatrix} \right)^2 \text{(A9)}$$

The difference between (A8) and (A9) is that the exchange constant $J$, which is antiferromagnetic in nature.
J_{AFM} = \left( -\frac{t_{pd1}}{U_1} - \frac{t_{pd2}}{U_2} \right) \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} + \frac{t_{pd1}}{U_1} + \frac{t_{pd2}}{U_2} - (t_{pd1}t_{pd2})^2 \\
\times \left[ \frac{1}{U_1(U_1 + \Delta \epsilon)} + \frac{1}{U_2(U_2 - \Delta \epsilon)} + \frac{1}{U} \left( \frac{1}{U_1} + \frac{1}{U_2} \right)^2 \right] \\
\times \begin{bmatrix} 1 & -1 \\ -1 & 1 \end{bmatrix} \right)^2 \right) \tag{A10}

In (A10), the RHS comprises of 2 × 2 matrices for which we consider the non-zero eigenvalue. The first term of (A10) is an identity matrix, while the matrix in the third term of (A10) has eigenvalue +2. The first term cancels with the second term (both corresponding to single hopping) and we obtain the final expression for J_{AFM} as,

\[ J_{AFM} = -2(t_{pd1}t_{pd2})^2 \]

\times \left[ \frac{1}{U_1(U_1 + \Delta \epsilon)} + \frac{1}{U_2(U_2 - \Delta \epsilon)} + \frac{1}{U} \left( \frac{1}{U_1} + \frac{1}{U_2} \right)^2 \right] \tag{A11}

**Appendix B. FM superexchange interaction**

The ferromagnetic superexchange which involves two orthogonal p-orbitals of the intermediate O^{2-} ion can be described by the Hamiltonian,

\[ H_{AFM} = \begin{bmatrix} 0 & 0 & t_{pd1} & 0 & t_{pd2} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & t_{pd1} & 0 & t_{pd2} & 0 & 0 & 0 & 0 & 0 \\ t_{pd1} & 0 & \tilde{U}_1 & 0 & 0 & 0 & t_{pd1} & 0 & t_{pd2} & 0 & 0 \\ 0 & t_{pd1} & 0 & \tilde{U}_2 & 0 & 0 & 0 & t_{pd1} & 0 & t_{pd2} & 0 \\ t_{pd2} & 0 & 0 & 0 & \tilde{U}_1 & 0 & 0 & 0 & t_{pd1} & 0 & t_{pd2} \\ 0 & 0 & t_{pd1} & 0 & t_{pd2} & 0 & \tilde{U} & -J_P & \tilde{U} & 0 & 0 \\ 0 & 0 & 0 & t_{pd1} & 0 & t_{pd2} & -J_P & 0 & \tilde{U} & 0 & 0 \end{bmatrix} \tag{B3}

Writing (B2) in block form,

\[ H_{FM} = \begin{bmatrix} H_{00} & T_{01} \\ T_{10} & H_{11} \end{bmatrix}, \quad H_{00} = 0, \quad H_{11} = \begin{bmatrix} \tilde{U}_1 & 0 & t_{pd1} \\ 0 & \tilde{U}_2 & t_{pd2} \\ t_{pd1} & t_{pd2} & \tilde{U} \end{bmatrix}, \tag{B4}

\[ T_{10} = \begin{bmatrix} t_{pd1} \\ t_{pd2} \end{bmatrix} = T_{01}^+ \]

Similarly writing (B3) in block form,

\[ H_{AFM} = \begin{bmatrix} H_{00} & T_{01} \\ T_{10} & H_{11} \end{bmatrix}, \quad H_{11} = \begin{bmatrix} \tilde{U}_1 & 0 & 0 & 0 \\ 0 & \tilde{U}_2 & 0 & 0 \\ 0 & 0 & \tilde{U}_1 & 0 \\ 0 & 0 & 0 & \tilde{U}_2 \end{bmatrix}, \quad H_{AFM} = \begin{bmatrix} \tilde{U}_1 & -J_P \\ -J_P & \tilde{U} \end{bmatrix}, \tag{B5}

In (B5), H_{00} is the 2 × 2 null matrix. The off-diagonal block matrices are,

\[ T_{10} = \begin{bmatrix} t_{pd1} \\ t_{pd2} \end{bmatrix} = T_{01}^+, \quad T_{21} = \begin{bmatrix} t_{pd1} & 0 & 0 & 0 \\ 0 & t_{pd1} & 0 & 0 \\ 0 & 0 & t_{pd1} & 0 \\ 0 & 0 & 0 & t_{pd1} \end{bmatrix} = T_{12}^+ \tag{B6}

Using the formula given in (A7) we obtain the effective Hamiltonian for the triplet case as

\[ H_{eff}^{FM} = -\left( \frac{t_{pd1}}{U_1} + \frac{t_{pd2}}{U_2} \right)^2 \tag{B7} \]
while for the singlet,
\[ H_{\text{eff}}^{FM} = \left( \frac{t_\text{pd11}}{U_1} + \frac{t_\text{pd22}}{U_2} \right) - \left( \frac{t_\text{pd11} + t_\text{pd22}}{J_p} \right)^2 \left[ \frac{v}{U_1} - \frac{j_p}{U_1 U_2} \right] \frac{v}{U_1 U_2} \frac{j_p}{U_1 U_2} \text{ } (B8) \]

Similar to appendix A, on subtraction of (B7) and (B8), the first terms in RHS cancel each other and we obtain the final expression for the ferromagnetic superexchange.

\[ J_{FM} = \left( \frac{t_\text{pd11} + t_\text{pd22}}{U - J_p} \right)^2 - \left( \frac{t_\text{pd11} + t_\text{pd22}}{J_p} \right)^2 \left[ \frac{v}{U_1} - \frac{j_p}{U_1 U_2} \right] \frac{v}{U_1 U_2} \frac{j_p}{U_1 U_2} \text{ } (B9) \]

The sign of \( J_{FM} \) is positive. Due to the lengthy expression for the eigenvalue of the matrix, the strength of FM superexchange interaction is obtained numerically.

\[ H_{FM} = \begin{bmatrix} 0 & t_{pd} & t_{pd} & 0 & 0 \\ t_{pd} & U & t_{pd} & t_{pp} & 0 \\ t_{pd} & t_{pd} & U & 0 & t_{pp} \\ 0 & t_{pp} & 0 & U & 0 \\ 0 & 0 & t_{pp} & 0 & U \\ 0 & t_{pd} & t_{pd} & 0 & 0 \end{bmatrix} \]

(B2)

Writing (B2) as a 3 \times 3 block matrix,
\[ H_{AFM} = \begin{bmatrix} H_{00} & T_{01} & T_{02} \\ T_{10} & H_{11} & T_{12} \\ T_{20} & T_{21} & H_{22} \end{bmatrix}, \quad H_{00} = 0, \quad H_{11} = \begin{bmatrix} U & t_{pd} & t_{pp} \\ t_{pd} & U & 0 \\ t_{pp} & 0 & U \end{bmatrix}, \quad H_{22} = \begin{bmatrix} U & 0 \\ 0 & 2U \end{bmatrix} \text{ } (C3) \]

The offdiagonal block matrices are,
\[ T_{10} = \begin{bmatrix} t_{pd} \\ 0 \end{bmatrix}, \text{ } T_{20} = \begin{bmatrix} 0 \\ t_{pd} \end{bmatrix}, \text{ } T_{21} = \begin{bmatrix} 0 & t_{pp} \\ t_{pp} & 0 \end{bmatrix}, \text{ } T_{12} = \begin{bmatrix} 0 \\ 0 \end{bmatrix} + \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \text{ } (C4) \]

After downfolding (using equation (A7)), the effective Hamiltonian for the triplet state is,
\[ H_{\text{eff}}^{FM} = -\frac{2t_{pd11}}{U + t_{pd}} - \frac{2t_{pd22}(t_{pd11}^2 + t_{pd22}^2)}{U(U + t_{pd})^2} \text{ } (C5) \]

For the singlet state of d-electron spins, there are in total sixteen states in Hilbert space. The ground states are \( d_{2s}^\uparrow c_{p1}^\uparrow c_{p1}^\downarrow c_{p1}^\downarrow c_{p1}^\uparrow d_{11}^\downarrow \), \( d_{2s}^\uparrow c_{p2}^\uparrow c_{p2}^\downarrow c_{p1}^\downarrow c_{p1}^\uparrow d_{11}^\downarrow \), \( d_{13}^\uparrow c_{p1}^\uparrow c_{p1}^\downarrow c_{p1}^\downarrow c_{p1}^\uparrow d_{11}^\downarrow \), \( d_{13}^\uparrow c_{p2}^\uparrow c_{p2}^\downarrow c_{p1}^\downarrow c_{p1}^\uparrow d_{11}^\downarrow \), \( d_{13}^\uparrow c_{p3}^\uparrow c_{p3}^\downarrow c_{p1}^\downarrow c_{p1}^\uparrow d_{11}^\downarrow \), \( d_{13}^\uparrow c_{p4}^\uparrow c_{p4}^\downarrow c_{p1}^\downarrow c_{p1}^\uparrow d_{11}^\downarrow \), \( d_{13}^\uparrow c_{p5}^\uparrow c_{p5}^\downarrow c_{p1}^\downarrow c_{p1}^\uparrow d_{11}^\downarrow \), and \( d_{13}^\uparrow c_{p6}^\uparrow c_{p6}^\downarrow c_{p1}^\downarrow c_{p1}^\uparrow d_{11}^\downarrow \). Similar to the case of spin-triplet, examples of the excited states are, a) \( d_{2s}^\uparrow d_{2s}^\downarrow c_{p1}^\uparrow c_{p1}^\downarrow c_{p1}^\downarrow c_{p1}^\uparrow d_{11}^\downarrow \) (single hopping process), b) state with an empty TM-site i.e., \( d_{1s}^\uparrow d_{1s}^\downarrow c_{p1}^\uparrow c_{p1}^\downarrow c_{p1}^\downarrow c_{p1}^\uparrow d_{11}^\downarrow \), and c) both TM sites are doubly

**Appendix C. Super-superexchange interaction**

The exchange interaction between the C\(^{3+}\) spins occurs via hopping through two O\(^{2-}\) ions, thus the Hamiltonian can be written as,
\[ H = - \sum_{\sigma=\uparrow,\downarrow} \sum_{i=1,2} [\epsilon \sigma \tilde{n}_i + \epsilon_i \tilde{n}_i \tilde{n}_i] \]
\[ -t_{pd}(d_{1s}^\uparrow c_{p1}^\uparrow + d_{2s}^\uparrow c_{p2}^\uparrow) - t_{pp} c_{p1}^\uparrow c_{p1}^\uparrow + h.c. \text{ } (C1) \]

In the above equation, \( t_{pp} \) corresponds to the hopping amplitude between the two O p-orbitals. Similar to appendices A and B, the ground state corresponds to two d-electrons with parallel spins or anti-parallel spins. The matrix form for parallel spins with corresponding basis states is,

\[ \begin{bmatrix} 0 & d_{2s}^\uparrow d_{2s}^\downarrow c_{p1}^\uparrow c_{p1}^\downarrow c_{p1}^\downarrow c_{p1}^\uparrow d_{11}^\downarrow & 0 \\ d_{2s}^\uparrow d_{2s}^\downarrow c_{p2}^\uparrow c_{p1}^\downarrow c_{p1}^\downarrow c_{p1}^\uparrow d_{11}^\downarrow & d_{2s}^\uparrow d_{2s}^\downarrow c_{p2}^\uparrow c_{p1}^\downarrow c_{p1}^\downarrow c_{p1}^\uparrow d_{11}^\downarrow & 0 \\ d_{2s}^\uparrow d_{2s}^\downarrow c_{p2}^\uparrow c_{p2}^\downarrow c_{p1}^\downarrow c_{p1}^\uparrow d_{11}^\downarrow & d_{2s}^\uparrow d_{2s}^\downarrow c_{p2}^\uparrow c_{p2}^\downarrow c_{p1}^\downarrow c_{p1}^\uparrow d_{11}^\downarrow & 0 \\ 0 & 2U & d_{2s}^\uparrow d_{2s}^\downarrow c_{p1}^\uparrow c_{p1}^\downarrow c_{p1}^\downarrow c_{p1}^\uparrow d_{11}^\downarrow & 0 \\ d_{2s}^\uparrow d_{2s}^\downarrow c_{p2}^\uparrow c_{p2}^\downarrow c_{p1}^\downarrow c_{p1}^\uparrow d_{11}^\downarrow & d_{2s}^\uparrow d_{2s}^\downarrow c_{p2}^\uparrow c_{p2}^\downarrow c_{p1}^\downarrow c_{p1}^\uparrow d_{11}^\downarrow & 0 \end{bmatrix} \]

occupied \( d_{2s}^\uparrow d_{2s}^\downarrow c_{p1}^\uparrow c_{p1}^\downarrow c_{p1}^\downarrow c_{p1}^\uparrow d_{11}^\downarrow \). Thus, due to the large number of states, we directly write the 16x16 matrix below in block form.

\[ H_{AFM} = \begin{bmatrix} H_{00} & T_{01} & T_{02} \\ T_{10} & H_{11} & T_{12} \\ T_{20} & T_{21} & H_{22} \end{bmatrix} = \begin{bmatrix} H_{00} & T_{01} & T_{02} \\ T_{10} & H_{11} & T_{12} \\ T_{20} & T_{21} & H_{22} \end{bmatrix} \text{ } (C6) \]

\[ H_{00} \text{ is a } 2 \times 2 \text{ diagonal matrix corresponding to the ground state on-site energy } 2\epsilon_d + 4\epsilon_p \text{ which is set to zero. The other block matrices along the diagonal are,} \]

\[ H_{11} = \begin{bmatrix} U & 0 & 0 \\ 0 & U & 0 \\ 0 & 0 & -t_{pp} \end{bmatrix}, \quad H_{22} = \begin{bmatrix} U & 0 \\ 0 & U \end{bmatrix}, \quad H_{33} = \begin{bmatrix} 2U & t_{pp} \\ t_{pp} & 2U \end{bmatrix} \text{ } (C7) \]
where $\tilde{T} = U + \Delta_{pd}$. The off-diagonal block matrices are given below.

$$T_{10} = \begin{bmatrix} t_{pd} & 0 \\ 0 & t_{pd} \end{bmatrix}, \quad T_{12} = \begin{bmatrix} 0 & 0 \\ 0 & 0 \end{bmatrix}$$

$$T_{13} = \begin{bmatrix} t_{pd} & 0 & 0 \\ 0 & t_{pd} & 0 \\ 0 & 0 & t_{pd} \end{bmatrix}$$

$T_{01} = T_{10}^T$, $T_{21} = T_{12}^T$ and $T_{31} = T_{13}^T$. The rest of the block matrices are null matrices. Using the method of downfolding, the effective Hamiltonian is given as,

$$H_{eff}^{FM} = -T_{01}H_{11}^{-1}T_{10} - T_{01}H_{11}^{-1}T_{12}H_{22}^{-1}T_{21}H_{11}^{-1}T_{10} - T_{01}H_{11}^{-1}T_{13}H_{33}^{-1}T_{31}H_{11}^{-1}T_{10}$$

The corresponding effective Hamiltonian of the singlet state is,

$$H_{eff}^{AFM} = \frac{2\tilde{t}_{pd}U}{\tilde{U}^2} \tilde{U} - \frac{2\tilde{t}_{pd}^2 \tilde{t}_{pp}}{\tilde{U}(\tilde{U}^2 - \tilde{U})^2} \begin{bmatrix} 1 & 1 \\ 1 & 1 \end{bmatrix}$$

$$+ \frac{2\tilde{t}_{pd}\tilde{U}}{(\tilde{U}^2 - \tilde{U})^3} \begin{bmatrix} \tilde{U} + \tilde{t}_{pp} & \tilde{t}_{pp} \\ \tilde{t}_{pp} & \tilde{U}^2 + \tilde{t}_{pp} \end{bmatrix}$$

(C10)

The final expression for the super-superexchange interaction strength, is the difference between equations (C10) and (C5). We obtain the full exchange term for super super exchange as,

$$\tilde{J}_{ss} = \frac{2\tilde{t}_{pd}^2 \tilde{U}}{\tilde{U}^3 + \tilde{U}^2 + \tilde{t}_{pd}} + \frac{2\tilde{t}_{pd} \tilde{t}_{pp}}{(\tilde{U}^2 + \tilde{U} - \tilde{U}^2)^2} - \frac{2\tilde{t}_{pd}^2 \tilde{t}_{pp}}{(\tilde{U}^2 + \tilde{U}^2)^2}$$

$$+ \frac{2\tilde{t}_{pd}\tilde{U}}{(\tilde{U}^2 - \tilde{U})^3} \begin{bmatrix} \tilde{U} + \tilde{t}_{pp} & \tilde{t}_{pp} \\ \tilde{t}_{pp} & \tilde{U}^2 + \tilde{t}_{pp} \end{bmatrix}$$

(C11)

The first two terms in RHS of (C11) are similar to single hopping process, except for the presence of $\tilde{t}_{pd}$ and $\tilde{t}_{pp}$ in the denominator. Since both, $\tilde{t}_{pd}$, $\tilde{t}_{pp}$ $\ll$ $\tilde{U}$, we neglect them in comparison to $\tilde{U}$, due to which the first two terms of (C11) get cancelled. In (C11), replacing the constant matrices by their eigenvalues,

$$\tilde{J}_{ss} = \frac{2\tilde{t}_{pd}^2 \tilde{U}^3}{(\tilde{U}^2 + \tilde{U}^2)^2} - \frac{2\tilde{t}_{pd}^2 \tilde{t}_{pp}}{(\tilde{U}^2 + \tilde{U}^2)^2}$$

$$+ \frac{2\tilde{t}_{pd}\tilde{U}}{(\tilde{U}^2 - \tilde{U})^3} \begin{bmatrix} \tilde{U} + \tilde{t}_{pp} & \tilde{t}_{pp} \\ \tilde{t}_{pp} & \tilde{U}^2 + \tilde{t}_{pp} \end{bmatrix}$$

(C12)

After obtaining the eigenvalue of the matrix in the above equation, the super-superexchange $\tilde{J}_{ss}$ constant can be calculated directly from (C12). Further simplification can be done, i.e. neglecting $\tilde{t}_{pp}^2$ in comparison to $\tilde{U}^2$ in the matrix and also the denominators of the second and third terms, resulting in,

$$\tilde{J}_{ss} = \frac{2\tilde{t}_{pd}^2 (\tilde{t}_{pd}^2 + \tilde{t}_{pp})}{\tilde{U}(\tilde{U} + \tilde{t}_{pd})^2} - \frac{2\tilde{t}_{pd} \tilde{t}_{pp}^2}{\tilde{U}^2} - \frac{2\tilde{t}_{pd}^2 \tilde{t}_{pp}}{\tilde{U}^3} + \frac{4\tilde{t}_{pd}^2 \tilde{t}_{pp}^2}{\tilde{U}^3}$$

(C13)

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