Orbital-selective behavior in cubanite CuFe$_2$S$_3$

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Using ab initio band structure calculations we show that mineral cubanite, CuFe$_2$S$_3$, demonstrates an orbital-selective behavior with some of the electrons occupying molecular orbitals of $x^2 - y^2$ symmetry and others localized at atomic orbitals. This is a rare situation for 3$d$ transition metal compounds explains experimentally observed absence of charge disproportionation, anomalous Mössbauer data, and ferromagnetic ordering in between nearest neighbor Fe ions.

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I. INTRODUCTION

In recent years there has been growing interest in investigating the ground state properties of transition metal (TM) compounds in which the orbital degrees of freedom play a dominant role.[6] Particularly interesting is the directionality of the d orbitals that can lead to the formation of various electronic and magnetic ground states, see e.g. Ref. [6]. Indeed, pronounced effects have been recently reported for many 4$d$ and 5$d$ metal cluster compounds revealing that different orbitals can behave in different ways, i.e. demonstrate orbital-selective behavior: orbitals directed toward neighbors in a TM dimer (or trimer) behave as delocalized and can be described by molecular orbitals, whereas the electrons in other orbitals are localized. This can result in a suppression of the effective magnetic moment and strongly affects the mechanism of exchange interaction. Thus, it turns out that the ground state properties of such cluster compounds are determined by their orbital structure and the related orbital-selective behavior.

However, in general such a situation is more typical for 4$d$ – 5$d$ systems, since a direct overlap between more spatially extended 4$d$ – 5$d$ orbitals is much larger than in case of 3$d$. In this respect, ternary chalcogenide compound CuFe$_2$S$_3$ (mineral cubanite) is a promising candidate for such study, since its electronic and magnetic ground state properties are far from being clear. CuFe$_2$S$_3$ crystallizes in the orthorhombic structure with a single class of Fe$_4$[6]. It was argued that iron has a nominal valency of +2.5, due to a “rapid electron exchange” between Fe$^{2+}$ (3$d^6$) and Fe$^{3+}$ (3$d^5$), giving an intermediate valency of about 2.5. Such fast electronic fluctuation would imply metallic conductivity, however, resistivity measurement on natural single crystal of CuFe$_2$S$_3$ have shown n-type semiconductor behavior.[14]

Magnetic measurements on CuFe$_2$S$_3$ show that cubanite is canted antiferromagnet (AFM) at low-temperature phase. Interestingly enough nearest iron neighbors inside a Fe–Fe dimer are coupled not antiferromagnetically as a conventional superexchange theory would suggest (see e.g. Ref. [15] or Ref. [16]), but ferromagnetically. The Fe–Fe dimers are coupled to each other antiferromagnetically.[15] The local magnetic moment was found to be $\sim 3.2 \mu_B$, i.e. somewhat smaller than what one would expect even for Fe$^{3+}$[16]

Motivated by the above mentioned physical aspects and in view of the current research activity on CuFe$_2$S$_3$ for several technological applications, we have investigated the ground state of CuFe$_2$S$_3$ using GGA and GGA+U calculations. We were able to unveil the ground

Figure 1: The crystal structure of CuFe$_2$S$_3$. FeS$_4$ (CuS$_4$) tetrahedra are shown in red (green) color. Two neighboring FeS$_4$ tetrahedra have a common edge.
state properties of CuFe$_2$S$_3$ and show that there are two types of $d$ orbitals in cubanite. First ones form molecular orbitals for two neighboring irons and electrons occupying these orbitals belong to both ions. Second are localized at atomic sites. This not only explains an intermediate valence 2.5$^+$ of Fe and anomalous results of Mössbauer measurements, but also elucidates the origin of the unexpected magnetic structure of this compound.

II. CRYSTAL STRUCTURE

The cubanite CuFe$_2$S$_3$ crystallizes within an orthorhombic structure (space group Pnma, $a = 6.23$ Å, $b = 11.11$ Å and $c = 6.46$ Å) with a quasi-hexagonal stacking of S$^{2-}$ anions where the cations are tetrahedrally coordinated (see Fig. 1). The structure is based upon a hexagonal close-packed network of S atoms with the cations in ordered, tetrahedral sites; the Cu atoms and 1/3 of the S atoms occupy the equipoint 4c (mirror planes), and the Fe atoms and remaining 2/3 of the S atoms are in the general positions, 8d. Experimental atomic positions and lattice parameters are taken from Ref. [11].

In orthorhombic cubanite Cu and Fe atoms are tetrahedrally coordinated by S atoms with two FeS$_4$ tetrahedra sharing their edges. This gives pairs of Fe ions with rather short distances between them. However, the distance of 2.81 Å, however, is too long to represent a chemical bond. It is also larger than that in KFeS$_2$, where tetrahedrally-coordinated iron atoms form chains with the Fe–Fe distance of 2.7 Å.

III. CALCULATION DETAILS

The ab initio band structure calculations of CuFe$_2$S$_3$ were carried out within the framework of density functional theory (DFT) implemented in VASP package. We used the generalized gradient approximation (GGA) and projector augmented wave (PAW) method. The exchange-correlation functional in Perdew-Burke-Ernzerhof (PBE) form was utilized. The cut-off energy was chosen to be 600 eV and the mesh of $6 \times 3 \times 6$ was used for integration over the Brillouin zone according to Monkhorst-Pack scheme. A non-interacting GGA Hamiltonian for the estimation of hopping integrals inside the Fe 3$d$ states was generated using the Wannier projection procedure in Quantum Espresso code on the same k-point grid. The correlation effects were taken into account via GGA+U approach as introduced in Ref. [27]. We chose the onsite Coulomb repulsion parameter to be $U=8$ eV and $U=6$ eV for Cu and Fe respectively, while the Hund’s rule coupling parameter ($J_H$) was taken as $J_H=0.95$ eV for both 3$d$ metal transition ions. The occupation numbers of Fe-3$d$ states were obtained by integration within atomic sphere with radius 1.302 Å. The crystal structure in GGA+U calculations was relaxed unless the interatomic forces were larger than 0.005 eV/Å.

IV. CALCULATION RESULTS

We start with the simplest non-magnetic calculations, which results are presented in Fig. 2. One might see that the bands extending from -2.7 to -1.5 eV correspond to Cu-3$d$ states, while Fe-3$d$ bands are between -1.5 to 2 eV. S-3$p$ bands are below -3 eV (not shown in Fig. 2a). There are 4 formula units in the unit cell used in the calculation. All twenty (twice degenerate due to spin) Cu-3$d$ bands are below the Fermi energy and therefore we see that Cu must be 1$^+$ (3$d^1$) in cubanite. The second important fact, which can be extracted from this type of calculations is that we see four lowest isolated Fe-3$d$ bands in energy range from -1.1 to -1.6 eV (Fig. 2a). Thus, there is one such band per each formula unit. A partial charge density corresponding to these bands shows that these are $e_g$ states ($x^2 − y^2$ orbitals in the local coordinate system, where the axis points to the centers of tetrahedron edges), see Fig. 3. One can also see that these are exactly two $d$ orbitals directed to each other in the common edge geometry of two FeS$_4$ tetrahedra.

This explains Mössbauer data, which do not show...
charge disproportionation between two irons, but observe a “rapid electron exchange” which is obviously a consequence of molecular orbitals formation. Moreover, one can see that there are two types of $d$ electrons in CuFe$_2$S$_3$ those forming molecular orbitals ($x^2 − y^2$) and others, which are expected to be localized at atomic sites. Thus, cubane could be an example of materials demonstrating orbital-selective behavior.

There are important implications of orbital-selective physics in CuFe$_2$S$_3$. E.g. in the case of odd number of electrons on $d$ shell the mechanism like double exchange stabilizes ferromagnetic exchange interaction for nearest neighbor Fe ions (those forming dimers Fe$_2$S$_6$ with a common edge of FeS$_4$ tetrahedra). Neglecting conventional superexchange one can readily see that the ferromagnetic configuration shown in Fig. 1 has the lowest total energy $E_0 = −20J_H − t$, where $t$ is a hopping parameter for electrons forming molecular orbitals and $J_H$ is the intra-atomic exchange. Antiferromagnetic order is impossible in this situation since one might have only one electron with given spin per site. This state is always lower in energy than the configuration with site-localized electrons of Fig. 1 (only antiferro version is shown; the ferro one has the same energy if one neglects super-exchange), $E_1 = −20J_H$. There also will be the configurations with two electrons occupying the molecular orbital, one of them is shown in Fig. 2, it is energy is $E_c = −16.5J_H − 2t$. Thus, we see that ferromagnetic “intra-dimer” order wins if $3.5J_H > t$, which is exactly the case of CuFe$_2$S$_3$, since $J_H ∼ 1$ eV and $t = 0.4$ eV as follows from our DFT calculations (the value of $t$ was taken from Wannier function projection).

This idea is very similar to a conventional double exchange: itinerant electrons with the $x^2 − y^2$ symmetry move from one Fe site to another and thereby substantially lowers the total energy (Fig. 3a). This is only possible if both Fe sites have the same spin projection. If there would be no such fluctuations, i.e. the system will be in configurations shown in Fig. 3b or Fig. 3c, there will be no such energy gain.

Figure 3: The partial charge density represented 4 separated Fe-3d bands on $[-1.1, -1.0]$ eV interval in a band structure on Fig 2a).

This discussion is in accord with direct magnetic GGA calculations, which results are presented in Table 1. The lowest in total energy is the configuration with Fe spins ordered ferromagnetically inside Fe–Fe dimers and maximally antiferromagnetic between them (configuration A). This result agrees with analysis of magnetic data performed in Ref. [17]. It also has to be mentioned a conventional superexchange mechanism between localized electrons tends to stabilize AFM order and is indeed operative for inter-dimer exchange interaction, while intra-dimer ferromagnetism is due to the formation of molecular orbitals, i.e. orbital-selective behavior.

Moreover we see that our GGA calculations are able to reproduce the correct magnetic ground state, and CuFe$_2$S$_3$ becomes insulating already in GGA approximation. The energy gap in configuration A is about 0.3 eV. Thus the ferromagnetic order of Fe spin moments in Fe-Fe dimers retains an additional itinerant electron for two irons ions within a dimer cluster.

In order to take into account correlation effects in CuFe$_2$S$_3$, we carried out GGA+$U$ calculations. The results are shown in Fig. 4 and displayed in Table 1. One can see that the band gap in GGA+$U$ increases up to about 0.8 eV in configuration A. The total energy calculations demonstrate that the state with FM dimer remains the lowest, see Table 1. The decrease of the energy difference

![Figure 4](image)

Table 1: The total energies ($E_{\text{tot}}$) and energy gap ($E_{\text{gap}}$) for the insulating states as obtained from GGA and GGA+$U$ ($U$(Cu)=8 eV, $U$(Fe)=6 eV) calculations for the different magnetic structures of CuFe$_2$S$_3$ (per formula unit). Notation are the same as in Ref. [17], corresponding magnetic configurations are presented in Fig. 2.

| Magnetic config. | GGA | GGA+$U$ |
|------------------|-----|---------|
|                  | $E_{\text{tot}}$, meV | $E_{\text{gap}}$, eV | $E_{\text{tot}}$, meV | $E_{\text{gap}}$, eV |
| A                | 0   | 0.3     | 0             | 0.8             |
| C                | 191.6 | 0.05   | 98.1          | 0.51            |
| AF dimers        | 262.6 | no     | 179.6         | no              |
| B                | 621.2 | no     | 335.4         | 0.35            |
between various configurations is related to the fact that now not Stoner-like exchange, but a much larger Hubbard $U$ correction defines the superexchange processes (in the denominator for the superexchange interaction).

The detailed analysis of the occupation matrices shows that the charge disproportionation does not occur even if all symmetry information is removed in the calculations. This suggests that molecular orbitals are not destroyed completely by the Hubbard correction (which tends to localize all electrons on atomic orbitals), but a more accurate methods such as e.g. cluster DFT+DMFT calculations should be used to study this effect. Moreover, lattice optimization also does not break the charge homogeneous state. Interestingly enough, we were able to obtain charge ordered solution in GGA+$U$ approach when Fe ions are coupled AFM in a Fe$_2$S$_6$ dimers, but its total energy is higher on 180 meV. In order to justify the validity of chosen $U$ parameters we repeat the calculations using smaller $U$(Fe)=4.5 eV, as e.g. in Ref. and $U$(Cu)=8 eV ($J_H$ on both ions is 0.95 eV). The results remain the same: the magnetic configuration A corresponds to the ground state, which is insulating with a band gap of ~1 eV. We obtain for other configurations have total energies of: 725 (B), 125 (C), and 400 (AFM dimers) meV. The ground state also does not change if one ignores Hubbard $U$ on Cu (it also retains insulating behavior).

V. CONCLUSIONS

We used ab initio calculations to study the physical properties of CuFe$_2$S$_3$. In transition metal compounds containing structural clusters of metals there can be realized a special state, when some of the electrons form singlet ($S = 0$) pairs, while others are effectively decoupled and may give e.g. a long-range magnetic order or stay paramagnetic. Our GGA calculations show that there are indeed two types of 3$d$-electrons in cubanite: those forming molecular orbitals ($x^2 - y^2$) and others, which are expected to be localized at atomic sites. This fact determines CuFe$_2$S$_3$ as a system with orbital-selective behavior. This in turn strongly affects magnetic properties of cubanite making exchange interaction between nearest neighbors strong and ferromagnetic (by “double-exchange-like” mechanism), while magnetic ordering between other iron ions is governed by the superexchange path.

The orbital-selective behavior also explains puzzling Mössbauer data, where no Fe separation onto Fe$^{2+}$ and Fe$^{3+}$, but a “rapid electron exchange” has been observed. We feel that our findings could be applied to explain the metallic high pressure phase of CuFe$_2$S$_3$, where Fe ions are surrounded by sulphur octahedra, forming dimers with a common face. In such a geometry $a_{1g}$ orbitals may take part in a strong molecular bonding leaving other electrons ($e_g$) site localized as it occurs in e.g. Ba$_5$AlIr$_2$O$_{11}$ or hexagonal structure such as Ba$_4$MeTM$_2$O$_9$ (where TM is a transition metal and Me is metal like Li, Na, La etc.). Of course this has to be checked by corresponding calculations on the high pressure phase of CuFe$_2$S$_3$. 

Figure 5: The schematic representation of the possible magnetic structures of CuFe$_2$S$_3$ discussed in Ref. with FM order in Fe–Fe dimers and one more with AFM order in Fe–Fe dimers considered in this paper.

Figure 6: The band structure (a) and partial densities of states (b) of CuFe$_2$S$_3$ obtained in GGA+$U$ approximation ($U$(Cu) = 8 eV, $U$(Fe) = 6 eV, $J_H$(Cu, Fe) = 0.95 eV). The bands with bonding-antibonding splitting of molecular orbitals are marked by red color, their character was deduced from the corresponding charge-density plots.
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