Half-metallic antiferromagnets in thiospinels

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We have theoretically designed the half-metallic (HM) antiferromagnets (AFMs) in thiospinel systems, Mn(CrV)S$_4$ and Fe$_0.5$Cu$_{0.5}$(V$_{0.5}$Ti$_{1.5}$)S$_4$, based on the electronic structure studies in the local-spin-density approximation (LSDA). We have also explored electronic and magnetic properties of parent spinel compounds of the above systems; CuV$_2$S$_4$ and CuTi$_2$S$_4$ are found to be HM ferromagnets in their cubic spinel structures, while MnCr$_2$S$_4$ is a ferrimagnetic insulator. We have discussed the feasibility of material synthesis of HM-AFM thiospinel systems.

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Since the first theoretical report of Heusler half-metallic (HM) ferromagnet NiMnSb by de Groot et al. [1], much effort has been devoted to developing the HM magnetic materials, in which the conduction electrons at the Fermi level E$_F$ are 100% spin-polarized [2]. Especially, the HM antiferromagnet (AFM) attracts great attention because it is a non-magnetic metal but its conduction electrons are 100% spin-polarized. It can be used as a probe of the spin-polarized scanning tunneling microscope without perturbing the spin-character of samples. Further, the HM-AFM is expected to play a vital role in the future spintronic devices that utilize the spin polarization of the carriers.

The first HM-AFM, V$_2$MnFe$_8$Sb$_7$In, which is a derivative of the Heusler compound, was proposed by van Leuken and de Groot [3]. Another possibility was suggested by Pickett [4] in the double perovskite system such as La$_2$V$_3$O$_8$. In this case, V and Mn have antiferromagnetically aligned magnetic moments that exactly cancel each other. To date, there has been no successful experimental realization of the HM-AFM.

The thiospinel FeCr$_2$S$_4$ in its metallic phase has the HM ferrimagnetic state with nominal valence configurations of Fe$^{2+}$ ($d^8$) and Cr$^{3+}$ ($d^3$) [5]. The magnetic moments of Fe and Cr are $4\mu_B$ and $-3\mu_B$, respectively, which produce the integer total magnetic moment of $-2\mu_B$ per formula unit. From this, one can expect that FeV$_2$S$_4$ becomes a HM-AFM, since V has one less electron than Cr and so the magnetic moment of two V$^{3+}$ ($d^2$: S=1) ions would cancel that of Fe$^{2+}$ ($d^6$: S=2), still possessing the HM property. Indeed the local-spin-density approximation (LSDA) band calculation yields the HM-AFM electronic structure of FeV$_2$S$_4$ [6]. Unfortunately, FeV$_2$S$_4$ does not exist in the cubic spinel structure but in the hexagonal NiAs structure (Cr$_3$S$_4$-type) with a complicated magnetic configuration [7]. So the above expectation does not work for FeV$_2$S$_4$ in nature.

Motivated by the above expectation, we attempt to search for the HM-AFM in other thiospinel compounds. Most of the thiospinel compounds of AB$_2$S$_4$-type (A, B: transition metals) with cubic structure have a ferrimagnetic ground state. Usually, the magnetic moment of the A ion in the tetrahedral site is antiferromagnetically polarized with that of the B ion in the octahedral site. Under this circumstance, there are some pairs of A and B which give rise to the exactly cancelled magnetic moment in AB$_2$S$_4$. Moreover, some spinels have the HM electronic structures, as in FeCr$_2$S$_4$. Then, by choosing proper pairs which satisfy these two conditions, one can devise the thiospinels with the HM-AFM nature. One possible pair is Mn($5\mu_B$) at A-site and mixed cations Cr($3\mu_B$)-V($2\mu_B$) at B-site. Another possible pair is Fe$_0.5$(2.5$\mu_B$)-Cu$_{0.5}$(0.0$\mu_B$) at A-site and V$_{0.5}$(1$\mu_B$)-Ti$_{1.5}$(1.5$\mu_B$) at B-site. Even though a pair like Fe(4$\mu_B$) and V(2$\mu_B$) can be chosen, they are not crystallized in the cubic spinel structure, as discussed above. For the same reason, the pairs such as [Co(3$\mu_B$) and Ti(1$\mu_B$)-V(2$\mu_B$)], and [Ni(2$\mu_B$) and Ti(1$\mu_B$)], are not suitable for a possible HM-AFM, because Ti and V form thiospinels only with Cu [8].

In this work, we will propose two candidates of HM-AFM in thiospinels with cubic spinel structure: Mn[CrV]S$_4$ and Fe$_0.5$Cu$_{0.5}$(V$_{0.5}$Ti$_{1.5}$)S$_4$. We show that electronic structures of these thiospinels have the HM-AFM nature, by using the LSDA on the basis of the linearized muffin-tin orbital (LMTO) band method. The von Barth-Hedin form of the exchange-correlation potential is utilized.

$\text{Mn[CrV]}S_4$ — We have performed the LSDA band calculation for a hypothetical spinel Mn[CrV]S$_4$. We used two formula units in the primitive unit cell. The primitive unit cell is formed by a cubic closed-packed (fcc) array of S atoms, in which one eighth of the tetrahedral and one-half of the octahedral interstitial sites are occupied by cations. S atoms have four-fold coordination, formed by three octahedral cations and one tetrahedral cation. For the LMTO calculation, four empty spheres are considered in the interstitial sites to enhance the packing ratio.

Figure 1 shows that Mn[CrV]S$_4$ has the HM-AFM ground state at the lattice constant $a = 10.110\text{Å}$ which is the experimental lattice constant of MnCr$_2$S$_4$. Spins of Cr and V are ferromagnetically aligned, but they are antiferromagnetically aligned to those of Mn. The energy gap is evident near $E_F$ in the spin-up density of states (DOS), and the DOS at $E_F$ originates mainly from spin-down V-3$d$ ($\sim$ two $t_{2g}$ electrons) states which will con-
Valence configuration of Mn$^{2+}$ occupied DOS suggests that Mn[CrV]S$_4$ which is a nature of the HM-AFM (Table I). In accordance with the present LSDA band result, the total magnetic moment becomes zero in the unit cell when the spinel structure with substituting V for Cr in MnCr$_2$S$_4$ is retained, the HM-AFM Mn[CrV]S$_4$ could be synthesized. The above experimental result may indicate that the bulk spinel phase of Mn[Cr$_{2-x}$V$_x$]S$_4$ would be unstable over $x = 0.6$. Then the possible attempt would be an artificial fabrication of Mn[CrV]S$_4$ film on appropriate substrates, which is desirable to be tested experimentally.

$F_{0.5}Cu_{0.5}[V_{0.5}Ti_{1.5}]S_4$ - We have mentioned that Fe$_2$V$_2$S$_4$, if it exists in the cubic spinel form, would be a strong candidate for the HM-AFM. We have also seen that V and Ti form thiospinels only with Cu: CuV$_2$S$_4$ and CuTi$_2$S$_4$.[17] On the basis of this, we have explored the combination of Fe, Cu, V, and Ti to make a...
thiospinel possessing both the HM and the AFM nature: Fe$_{0.5}$Cu$_{0.5}$[V$_{0.5}$Ti$_{1.5}$]S$_4$ (FCVTS). We have performed the LSDA electronic structure calculation for FCVTS by replacing V$_{0.5}$Ti$_{1.5}$ with a virtual atom having atomic number 22.25. The lattice constant of $a = 9.8865\text{"A}$ is used which is interpolated from end members, CuV$_2$S$_4$ and CuTi$_2$S$_4$. As shown in Fig. 3, FCVTS really has the HM-AFM electronic structure. Ten Cu 3$d$-states and five spin-down Fe 3$d$-states are fully occupied. The DOS at $E_F$ originates from spin-up Fe 3$d$ ($\sim e_g$) and V$_{0.5}$Ti$_{1.5}$ 3$d$ ($\sim t_{2g}$) states. The calculated magnetic moments in Table II reflect that the valence configuration of FCVTS corresponds to Fe$_{0.5}$Cu$_{0.5}$[V$_{0.5}$Ti$_{1.5}$]$^{3.25+}$S$_4^2$ with zero total magnetic moment. The magnetic mechanism in FCVTS can be understood in a similar way to the case in Fe$_{0.5}$Cu$_{0.5}$Cr$_2$S$_4$.[F4]

Now, let us discuss the possibility of synthesizing FCVTS. We first consider parent thiospinels, CuV$_2$S$_4$ and CuTi$_2$S$_4$, both of which have metallic nature.[F6]

The LSDA band calculation shows that the CuV$_2$S$_4$ has a HM ground state in its cubic spinel structure (Fig. 4). But, this result does not coincide with experimental results for CuV$_2$S$_4$ having no spontaneous magnetic property. In fact, CuV$_2$S$_4$ has a CDW-type phase transition below 90 K. Accordingly, the cubic unit cell is transformed to a tetragonal structure which is induced by the Jahn-Teller local small distortion at the V site [17–21]. Our result suggests that if CuV$_2$S$_4$ exists in the cubic spinel structure, it will have a HM ferromagnetic ground state. The oxidation state of Cu atoms of CuV$_2$S$_4$ is closer to Cu$^{2+}$.[F22] The bands near $E_F$ are predominantly of V 3$d$ character, so that the metallic nature of CuV$_2$S$_4$ comes mainly from the V atom.[F22]

The CDW-type phase transition can be suppressed by the random occupation of the octahedral sites in the spinel structure. Indeed, Cu[V$_{1.9}$Ti$_{0.1}$]S$_4$ showed no evidence of a phase transition due to random occupation of the octahedral sites by the V-Ti mixture [23]. CuV$_2$S$_4$ has a large susceptibility due to considerable exchange enhancement [22]. The ferromagnetism in the Cr-mixed Cu$_2$V$_2$S$_4$ compound Cu$_{2-x}$Cr$_x$S$_4$ at low Cr concentrations is considered to come from the large susceptibility of CuV$_2$S$_4$ [23]. Therefore, one can also expect that, if some of Cu atoms are replaced by Fe atoms, (FeCu)V$_2$S$_4$ would become a ferromagnet.

CuTi$_2$S$_4$ shows a metallic behavior [24] and the weak magnetism [23]. Our LSDA band calculation also indicates that both the metallic nature and the weak mag-
netism of CuTi$_2$S$_4$ result from 3$d$-bands of Ti ions (Table. [3]). As shown in Fig. 3, the CuTi$_2$S$_4$ also has a HM ferromagnetic ground state. The electronic configuration of Cu at the A-site is considered to be close to $e_g^{4}t_{2g}^{6}$ ($S=0$). Combining the above features, one can make a metallic Cu[V$_{0.5}$Ti$_{1.5}$]S$_4$ having a large susceptibility.

Then by mixing Fe ions with Cu[V$_{0.5}$Ti$_{1.5}$]S$_4$ to have exact cancellation of magnetic moments, one can possibly make HM-AFM FCVTS. In conclusion, we have predicted that Mn[CrV]S$_4$ and FCVTS satisfy two criteria for the HM-AFM: the antiferromagnetic couplings between magnetic moments and the HM property. The possibility of synthesizing HM-AFMs is discussed by considering electronic, transport, and magnetic properties of parent thiospinel compounds. MnCr$_2$S$_4$ found to be a ferromagnetic insulator in agreement with experiment, while CuV$_2$S$_4$ and CuTi$_2$S$_4$ are found to be HM ferromagnets in their cubic spinel structures.

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FIG. 5. Total and PLDOS of CuTi$_2$S$_4$.

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