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2009 J. Phys.: Condens. Matter 21 445803

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A study of the disordered dilute magnetic semiconductors $\text{Zn}_{1-x}\text{Cr}_x\text{Se}$ and $\text{Zn}_{1-x}\text{Fe}_x\text{Se}$

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Received 7 May 2009, in final form 7 September 2009

Published 15 October 2009

Online at stacks.iop.org/JPhysCM/21/445803

Abstract

We report on the electronic structure and exchange interactions in the dilute magnetic semiconductors $\text{Zn}_{1-x}\text{Cr}_x\text{Se}$ and $\text{Zn}_{1-x}\text{Fe}_x\text{Se}$. The exchange energies and densities of states were obtained using the layer Korringa–Kohn–Rostoker method and the coherent potential approximation. We find that the dominant exchange in all cases is the super-exchange mechanism, and it is found to be antiferromagnetic for $\text{Zn}_{1-x}\text{Fe}_x\text{Se}$ at all concentrations. For $\text{Zn}_{1-x}\text{Cr}_x\text{Se}$ the exchange interaction changes from ferromagnetic to antiferromagnetic at high concentrations due to the ability of Cr in the antiferromagnetic state to more effectively bond with the host structure. The strength of the super-exchange coupling in the tight binding model is linear in concentration, which we observe for $\text{Zn}_{1-x}\text{Fe}_x\text{Se}$. However, as in the case of $\text{Zn}_{1-x}\text{Cr}_x\text{Se}$, when the chemical and magnetic interactions are strongly coupled this simple scaling is no longer observed.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

There is considerable interest in developing ferromagnetic (FM) dilute magnetic semiconductors (DMS) for spintronic applications. Of the different classes of DMS materials previously studied (II–VI, III–V, IV–VI etc) only a few have been found to exist ferromagnetically at room temperature. Some of these include GaMnN [1], TiCoO₂ [2], ZnCoO [3] and ZnCrTe [4]. It is important, in particular, to study the mechanism(s) involved in the magnetic coupling and how they are dependent on the type of magnetic ion, the ion's spacing and concentration, and the semiconducting host.

The magnetic behavior of the II–VI DMS materials has been widely confirmed to be a product of indirect sp–d interactions between the TM and the host [5–9] which could either be a product of a super-exchange (SE) [10, 11] or a double-exchange (DE) [12, 13] mechanism. The DE is a FM process in which the kinetic energy is lowered through the formation of a sp–d resonant state between the TM-d state and the sp states of the conduction band (CB). While the SE is a kinetic p–d exchange and occurs when an anion-p-electron hops to an empty neighboring TM-d state which allows the newly unpaired p-electron to couple antiferromagnetically with the other adjacent TM. The SE is antiferromagnetic (AFM)

for TMs with at least a half-filled d-shell and can be either FM or AFM for TMs with less than a half-filled d-shell. The strength of the SE is regulated by the crystal structure, p–d promotion energy of the transferred electron and the level of sp–d hybridization. The strength of the DE scales with the population of TM-d states at the Fermi energy.

It is often unclear as to which of these mechanisms is the dominant exchange interaction. In a previous *ab initio* study [14] it was found that the SE and the DE could coexist. It was also shown that a crystal field split t_{2g} d-orbital exhibited greater hybridization over the e_g d-orbitals due to the orientation of each type of d-orbitals with respect to the host crystal. $\text{Zn}_{1-x}\text{Cr}_x$ (S, Se, Te) exhibits this p- t_{2g} hybridization, while $\text{Zn}_{1-x}\text{Fe}_x$ (S, Se, Te) exhibits the weaker p- e_g hybridization. The SE is therefore predicted to produce a FM coupling in the Cr doped semiconductors, and an AFM coupling in the Fe doped semiconductors.

Tight binding approaches predict that the DE and SE interactions will strengthen with increasing TM concentration [15, 16]. This model predicts the DE scales as the bandwidth of the TM d-peak located in the gap, or as \sqrt{x} , where x is the concentration of the TM. However, when the Fermi energy (FE) lies between the manifold of the e_g and t_{2g} TM-d states the SE becomes dominant. The SE lowers the energy

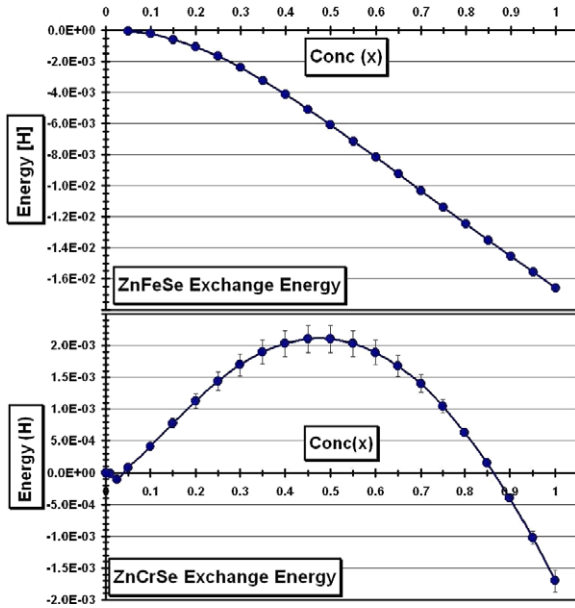


Figure 1. The exchange energy as a function of concentration for $\text{Zn}_{1-x}\text{Fe}_x\text{Se}$ (top) and $\text{Zn}_{1-x}\text{Cr}_x\text{Se}$ (bottom).

by increasing the exchange splitting between the occupied and unoccupied d-orbitals. The SE scales as x since the number of shifted orbitals scales as x [16]. It was shown in this model that when the FE lies off-center of a TM-d peak a competition between the DE and SE is also likely to exist.

In this study we vary the concentration of the TM in $\text{Zn}_{1-x}\text{Cr}_x\text{Se}$, and $\text{Zn}_{1-x}\text{Fe}_x\text{Se}$. By examining the DOS we will be able to confirm whether the material is half-metallic, and examine how the parameters that govern the strength of the DE and SE change with concentration. In particular we examine the tight binding prediction for the behavior of the exchange mechanisms as the concentration is varied. With the aid of the DOS we will also examine the bonding in different magnetic configurations and how that impacts the magnetic interactions. This analysis will explain the AFM behavior of $\text{Zn}_{1-x}\text{Fe}_x\text{Se}$ over all concentrations of Fe and help explain the change from a FM to AFM coupling observed in $\text{Zn}_{1-x}\text{Cr}_x\text{Se}$. It will be shown that at high concentrations the magnetic state of the TM will affect the stability of the crystal bonding and that if a magnetic d-orbital is able to simultaneously facilitate the crystal bonding along with the p-d exchange, the exchange energy will increase ($\text{Zn}_{1-x}\text{Fe}_x\text{Se}$) while if the chemical and magnetic interactions are in competition, the exchange will not be represented by a simple scaling in concentration ($\text{Zn}_{1-x}\text{Cr}_x\text{Se}$).

2. Computational details

The calculation of the electronic structure and exchange energy were performed in the local density approximation using the layer Korringa-Kohn-Rostoker approach [17]. We also incorporated the coherent potential approximation (CPA) [18] which allows one to model disordered crystals. The calculations were performed by stacking layers along the [100] direction, which simulates the TMs placed one lattice

constant apart. The two-dimensional layer unit cell was calculated from the experimental lattice constant of 5.74 Å and was kept constant for all calculations. Equal size Wigner-Seitz spheres were used to model the host and TM while empty spheres were placed in the two high symmetry interstitial sites. The exchange energy was obtained using the Force theorem [19, 20] which allows one to determine the total energy difference by virtue of the band sum energies, provided the same potential (frozen) is used for both magnetic configurations.

3. Exchange energy

$\text{Zn}_{1-x}\text{Cr}_x$ (VI) is expected to exhibit FM interactions, since both the DE and SE are both FM. For Cr the possibility of an AFM or FM SE exists since the TM's d-shell is less than a half-filled shell. This type of electronic configuration allows, the possibility of a majority (FM) or minority (AFM) spin p-d transfer during the SE. The simple explanation, for a favored FM SE in Cr, is that when a majority p-electron is transferred, the spin S on the TM is maximized, lowering the ground state energy in accordance with Hund's rules. The more in depth explanation comes from the Kanamori model [21] which predicts that the energy, resulting from a majority transferred d-electron (FM SE), is lower than the minority d-electron transfer (AFM SE) by $4J$, where J is the energy required to align spins from different orbitals. In contrast, by applying similar rules, $\text{Zn}_{1-x}\text{Fe}_x\text{Se}$ should exhibit an AFM SE since the d-shell is over half-filled and only a spin-minority 4p-electron can be transferred.

The exchange energy in figure 1 for $\text{Zn}_{1-x}\text{Fe}_x\text{Se}$ (top pane) is indeed found to be AFM, and monotonically becoming stronger as the concentration increases. Since Fe has e_g states at the FE the DE (FM) and SE (AFM) are both possible. The almost linear behavior is consistent with the tight binding models referred to earlier, which stated that the DE scales as \sqrt{x} while the SE scales as x . Since the exchange is AFM and the behavior is close to linear for most of the concentration range the super-exchange is the controlling exchange mechanism in $\text{Zn}_{1-x}\text{Fe}_x\text{Se}$.

In $\text{Zn}_{1-x}\text{Cr}_x\text{Se}$ (bottom pane) the exchange energy is nearly linear at low concentrations which indicates that the SE is also the controlling mechanism. However, the behavior of the exchange energy for $\text{Zn}_{1-x}\text{Cr}_x\text{Se}$ for the entire concentration range is somewhat unexpected. At around 50% the exchange energy begins to level off and then decrease. What is even more surprising is the rate at which the exchange energy decreases. At 85% the exchange interaction is now AFM and still rapidly decreasing. In order to fully explain why $\text{Zn}_{1-x}\text{Cr}_x\text{Se}$ is becoming strongly AFM we must look beyond the simple exchange view that separates chemical and magnetic interactions. This simple model would predict a positive and nearly linear behavior of the exchange energy, since the SE and the DE are expected to be both FM. We must look at how each magnetic configuration affects the crystal bonding. Clues that this interaction is relevant can be found in the fact that the ground state crystal structure of ZnSe is zincblende while the ground state structure of CrSe

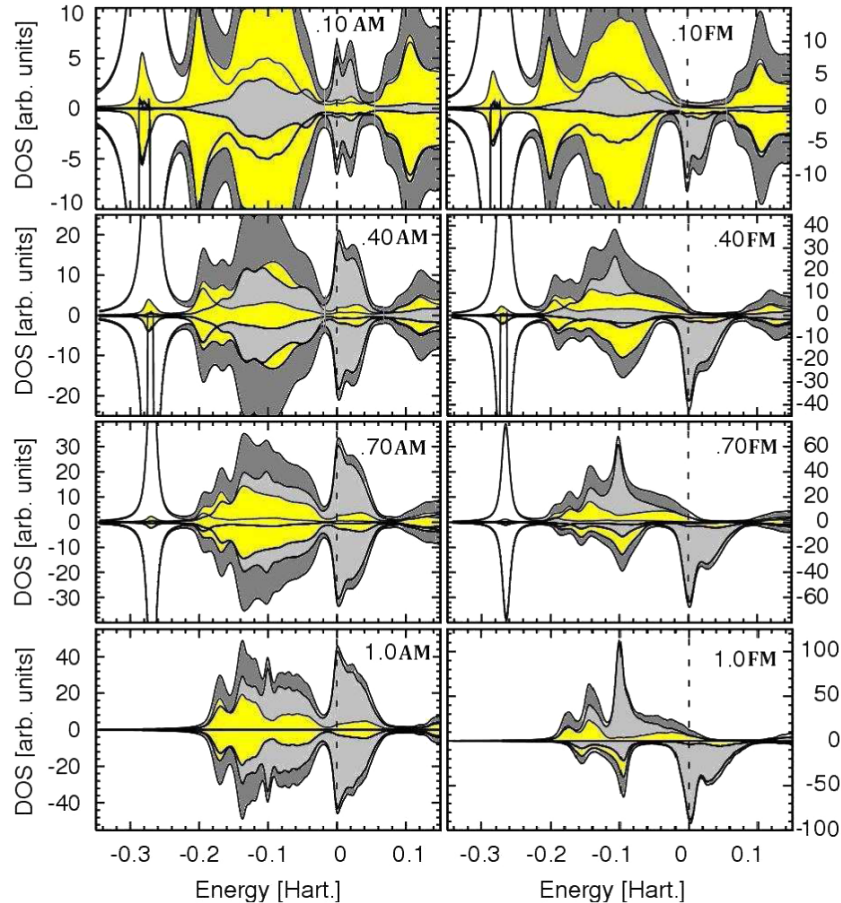


Figure 2. The total and partial DOS of $Zn_{1-x}Fe_xSe$. The energy has been shifted so that the FE lies at $E = 0$. The darker shade is the total DOS while the medium shade is the Fe states, the light shade is the Se states and the white shade is the Zn states.

is the NiAs hexagonal structure (hP4). CrSe has been found to exhibit a metastable zincblende state that is stable up to a few monolayers [22–24]. In contrast FeSe will naturally form in a distorted CuAu structure (tP4) [25]. The tP4 structure is similar to the zincblende structure in that they are both tetragonally bonded. The DOS will aid us in understanding how TM bonding affects the exchange energy. The strength of the SE will be determined by the amount of hybridization or bonding between the TM-d states and the host crystal. This can be inferred from the broadening of states.

4. Density of states

4.1. $Zn_{1-x}Fe_xSe$

When the TM is added, to the semiconducting host, the d-shell of the TM is split by the tetragonal crystal field into e_g and t_{2g} states with the former lying lower in energy. These states, if they coincide in energy with the semiconductor's valence band, can interact and broaden out into bands which typically lose the signature of crystal field split d states. In the zincblende structure, the e_g states point along the coordinate axes and overlap slightly with the anion's orbitals forming the π bonds. The t_{2g} states form the stronger σ bonds of the crystal since they point towards the anion sites resulting in a more

substantial pd overlap. Thus the e_g states will remain narrow with little anion p-admixture even when they lie within the valence band, whereas the t_{2g} states from a broad band with significant amounts of anion p-orbital hybridization. The t_{2g} states will be more important in forming crystal cohesion as the TM concentration is increased. There are also nonbonding TM d states that can be occupied and lie in the band gap of the semiconductor. The peaks are narrow in nature, and will still show the characteristic of crystal field split orbitals. The bonding interactions of a TM embedded in a semiconducting host has been well documented, for example, in the work of Zunger *et al* [26].

The DOS for $Zn_{1-x}Fe_xSe$ is shown in figure 2. Since Fe has six d-electrons we see, as expected, filled majority e_g and t_{2g} states as well as a single minority electron in the lowest e_g state. The AFM DOS for several TM concentrations is shown on the left hand pane while the corresponding FM cases are shown on the right. In the FM figures we see a narrow minority e_g state at the Fermi energy and an unoccupied minority t_{2g} states. The latter shows some anion p state mixed in. These features remain relatively unchanged as the concentration of Fe increases. Without any hybridization and bonding we would expect a spin moment of 4, however interactions with the host crystal reduce that moment to roughly 3. As the concentration is increased we see the VB majority states broaden and have

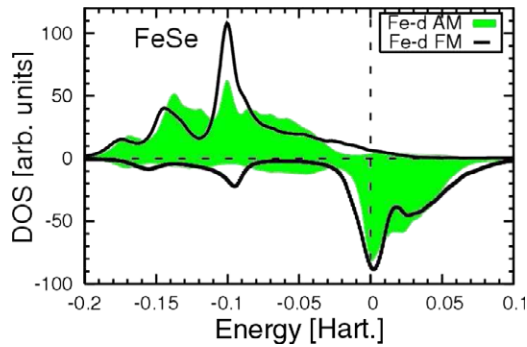


Figure 3. The onsite DOS of a single FeSe for both the AFM (shaded) and FM (bold line) orientations.

some weight above the FE. This increases the presence of bonding minority states inside the VB, thereby reducing the moment. Hybridization and broadening, especially in the t_{2g} bands, result in less than 5 majority Fe d states and more than 1 minority Fe d-electron. Using symmetry arguments we can identify whether the TM-d state is of e_g or t_{2g} type. The absence of anion p-orbitals around -0.1 Ha in the majority band indicates that the narrow TM-d peak at this energy has an e_g symmetry. Above and below -0.1 Ha the number of anion p states increase indicating that these broad TM-d peaks have a t_{2g} symmetry. As the concentration of Fe is increased, in the FM state, these features inside the VB remain sharp. This indicates that Fe does not bond effectively in the FM crystal.

Now we examine the AFM DOS profiles for these same concentrations. The ground state is expected to be AFM based upon super-exchange arguments with the anion p-electron hopping into an e_g minority orbital in accordance with Hund's rules. The occupied Fe d states show hybridization to a greater degree than in the FM case again indicative of a more stable state. The effectiveness of the SE is inferred when we see hybridization. We can see this in more detail in figure 3, which shows the onsite DOS for the single Fe atom at $x = 1.0$. The solid line represents the FM DOS. The sharp e_g peak is clearly visible in both majority and minority spin channels. The AFM case, shaded, shows a smaller, broader e_g feature, and a broader set of t_{2g} states. In the dilute limit the magnetic and chemical interactions can be viewed independently since at small concentrations, the Zn atoms dominate the cation contributions to the crystal cohesion. However, as the concentration is increased, the Fe atoms play an increasingly important role in bonding the crystal, and the magnetic and chemical interactions become interrelated. In the case of Fe, both magnetic and chemical interactions are controlled by the partially occupied minority e_g d states which produce weaker π bonds with the anion. The increased broadening of the AFM DOS is indicative of the interactions involved in AFM super-exchange. Super-exchange, with the hopping of an anion electron into the unoccupied minority e_g state, is consistent with Fe π bonding. Since the TM-d states broaden significantly in the AFM DOS, and since the AFM SE does not disrupt the π bonding between the TM and the host, or visa-versa, the SE and chemical bonding can be considered as independent interactions. Therefore the AFM

coupling of the super-exchange is expected to increase roughly linearly with concentration, as predicted by the tight binding model discussed previously. This is exactly what we observe in figure 1.

4.2. $Zn_{1-x}Cr_xSe$

As seen in figure 1, the exchange energy versus concentration for Cr behaves differently than for Fe. The exchange starts off ferromagnetic, increases reaching a maximum around 50%, then subsequently decreasing and finally becoming antiferromagnetic. We will use the density of states to explain this behavior. Cr has two fewer d-electrons than Fe, and its four electrons fill the lower lying e_g states and partially fill the majority t_{2g} states. Due to the hybridization effects, the calculated moment in $Zn_{1-x}Cr_xSe$ is slightly less than the atomic moment of four, but much nearer to the atomic value than what was observed for Fe.

Figure 4 shows the AFM and FM DOS profiles for $Zn_{1-x}Cr_xSe$ for various concentrations of Cr. Examining the FM DOS we can again see the mostly unoccupied e_g and t_{2g} minority states. As the concentration of Cr is increased we see that the d-orbitals shift closer to the Fermi energy. The broadening of the majority Cr t_{2g} states into the gap results in a decrease in the number of majority t_{2g} Cr states and an increase in the number of minority e_g Cr states. The majority Cr d states within the valence band show a partially occupied t_{2g} band and a narrower e_g peak. The features of these peaks remain relatively constant as the concentration is increased in the FM DOS. Lower lying d states sharpen as the concentration of Cr is increased as a result of fewer Zn sp states with which to hybridize. This is in contrast to the AFM DOS profile where increasing the Cr concentration causes a significant broadening in the Cr majority d states.

Figure 5 shows the onsite DOS profiles for FM and AFM cases at $x = 1.0$. The FM case shows a distinct e_g majority peak and t_{2g} majority band (solid line), while in the AFM case (shaded curve), we can see broader features with the majority e_g state forming a shoulder on the broad t_{2g} band. This behavior is indicative of a more effective crystal bonding. Some minority states can also be seen just below the Fermi level in the AFM DOS profile which is indicative of the SE transferring anion minority p-electrons.

As was the case for Fe, in the dilute limit the crystal cohesion comes from Zn sp^3 hybrid states overlapping with the Se p states. The coupling of Cr ions in the dilute limit is again determined by the super-exchange mechanism, with double-exchange also possible since there is a conducting channel at the Fermi level. In the SE model the anion p-electron can either occupy a majority t_{2g} state or a minority e_g state. The former would be favored by Hund's rules since it would maximize S . This would lead to ferromagnetic coupling as observed. However, as the concentration of Cr is increased, the super-exchange plays an increasing role in the crystal cohesion. In this case, because of the particular electronic structure of Cr with its single hole in the majority t_{2g} shell, an anion p-electron hopping into a t_{2g} shell during SE would fill the d-shell. This electronic filling would lead to an

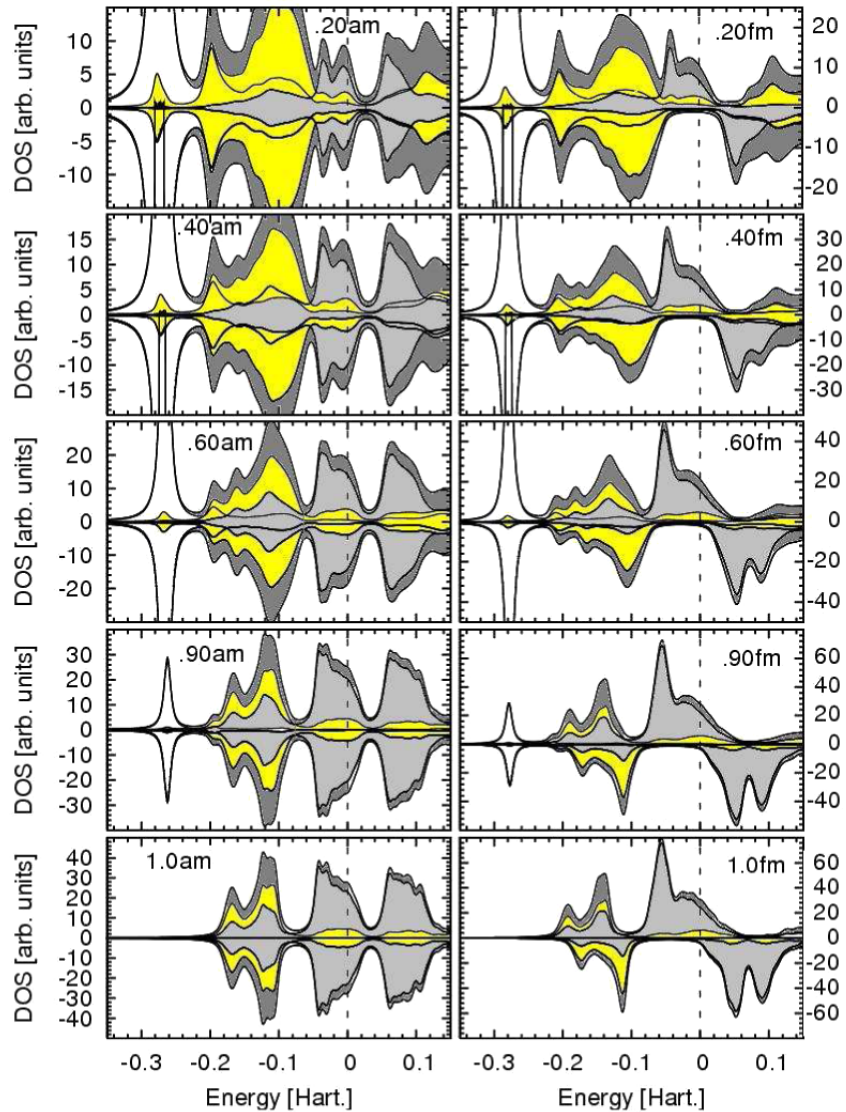


Figure 4. Total and partial DOS of $Zn_{1-x}Cr_xSe$. The energy has been shifted so that the FE lies at $E = 0$. The darker shade is the total DOS while the medium shade is the Fe states, the light shade is the Se states and the white shade is the Zn states.

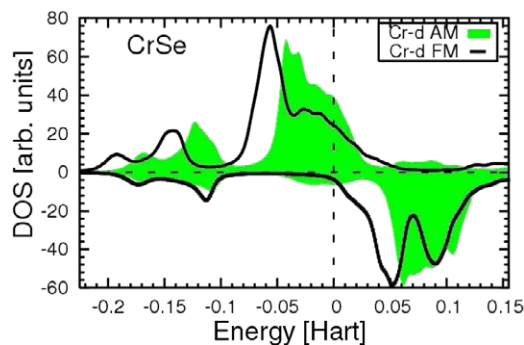


Figure 5. The onsite DOS of a single CrSe for both the AFM (shaded) and FM (bold line) orientations.

orbital that would be relatively inert and unable to participate effectively in the crystal bonding. The minority d states would remain predominantly unoccupied too and also therefore be

unable to contribute to the crystal bonding. If, however a minority anion p-electron hopped into the unoccupied e_g state it would still allow the partially occupied majority t_{2g} orbitals to participate in chemical bonding. In this case, the SE would produce an AFM coupling. Because of the particular electronic configuration of Cr the FM SE is incompatible with effective crystal bonding at large concentrations. Therefore the magnetic coupling will change from FM to AFM as the concentration of Cr is increased. This behavior coincides with the observations of figure 1 that above a concentration of 50% the exchange energy is decreasing in such a fashion that at 85% the AFM state has become more favorable.

5. Conclusion

Our study indicates that in the dilute limit the magnetic coupling is independent of crystal bonding, and in the case of both systems studied, $Zn_{1-x}Cr_xSe$ and $Zn_{1-x}Fe_xSe$, the

SE predicts the magnetic ground state. The strength of the exchange coupling has been observed to be consistent with the tight binding model at small concentrations. However, as the concentration is increased, the TM must also fulfil the role of chemical bonding in the crystal. In the case of Fe, the role of the bonding agent can be fulfilled without hindering the magnetic exchange. This characteristic of Fe results in the exchange energy monotonically decreasing for all concentrations, as predicted by the tight binding model. However in Cr, the usual dilute limit SE, which is FM, produces a state that does not bond effectively. As a result, we find the AFM configuration of $\text{Zn}_{1-x}\text{Cr}_x\text{Se}$, which would not be normally favored energetically in the dilute limit, becomes necessary at high concentrations to allow for a more effective chemical bonding.

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