Spin-polarization in half-metals

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Half-metals are defined by an electronic structure, which shows conduction by charge carriers of one spin direction exclusively. Consequently, the spin polarization of the conduction electrons should be 100%. In reality this complete spin polarization is not always observed. Since the experimental search for half-metals is tedious and the verification of the expected spin polarization is involved, electronic structure calculations have played an important role in this area. So, an important question is, how the approximations in such calculations influence the resulting spin polarization of the conduction. Another aspect is the well-known fact that bulk properties can be very different from surface and interface properties. Indeed, measurements of the spin polarization in the bulk for, e.g., NiMnSb, show results different from surface sensitive measurements. In this respect it is important to realize that the origin of half-metallic behavior is not unique. Consequently, the deviations from the bulk behavior at the surface/interface can be important. Three different categories of half-metals can be distinguished and their expected surface properties will be discussed. Finally, ways will be described to control the properties at interfaces.
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I. CLASSIFICATION OF HALF-METALLIC SYSTEMS

Half-metals are defined as magnetic materials showing a band gap at the Fermi energy for one spin direction. Consequently only charge carriers of one spin direction contribute to the conduction. Since the band gap is the essential ingredient in half-metals, it is important to consider its origin. Dozens of half-metals are known by now. Three categories can be distinguished on the basis of the nature of the band gap: half-metals with (1) covalent band gaps, (2) charge-transfer band gaps, and (3) $d-d$ band gaps. This distinction is important because the origin of the half-metallicity is different in each category. Hence the influence of external perturbations (e.g., pressure) is different as well as the sensitivity to disorder, behavior at surfaces and interfaces, etc.

A. Covalent band gaps

The origin of the band gap in this category is strongly related with well-known semiconductors of group III–V type, like, e.g., GaAs. A well-known example is NiMnSb.[1] It crystallizes in the Heusler $C1_b$ structure, which is closely related with the zincblende structure: One of the empty positions is occupied by the third consistuent (Ni) here. Like in the group III–V semiconductors, the crystal structure is essential, but also the proper site occupation is important: Both Mn and Sb have to occupy sites with tetrahedral coordination. The band structure, interactions, and bonding for the semiconducting spin direction are very much equivalent to that in the group III–V semiconductors, with which it is pseudoiso-electronic. The presence of occupied d minority states is essential: half-metals in this category are weak magnets.[2] The metallic spin direction shows conduction in very wide bands with an effective mass approximately equal to the free electron mass. Many half-metals in this category could be imagined, e.g., zincblende MnAs.[3] However, the zincblende structure is not the stable one for this compound.[3]

B. Charge-transfer band gaps

This category is found in strongly magnetic compounds, where the d bands of the transition metal are empty for the minority spin direction and the itinerant s,p electrons of the transition metal have been localized on the anions. Examples of half-metals in this category are CrO_2,[4] the colossal magnetoresistance (CMR) materials[5] and double perovskites.[6] The occurrence of the band gap (for one spin direction) is not very dependent on the crystal structure. Naturally, compounds in this category are strong magnets.

C. Materials with a $d-d$ band gap

Half-metals in this category show rather narrow bands, so that gaps occur between crystal-field split bands. The exchange splitting can be such that the Fermi level is posi-

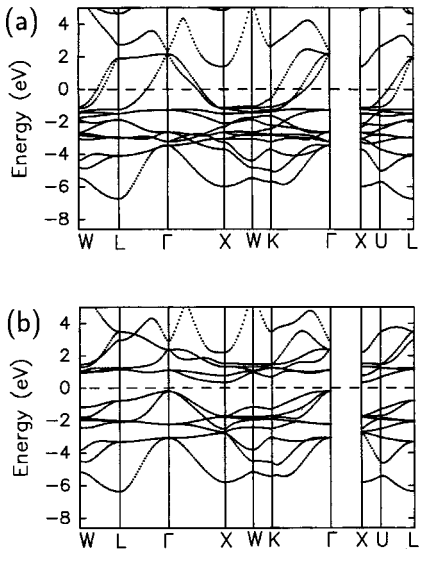

FIG. 1. Band structure of NiMnSb. (a) Majority spin channel and (b) minority spin channel. The Fermi level is at 0.

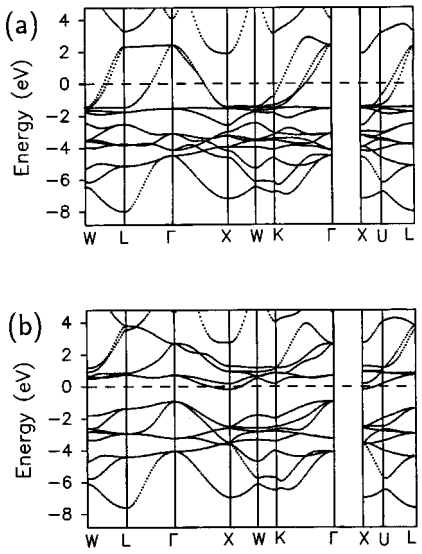

FIG. 3. Band structure of NiMnSb at the density of Ni_2MnSb. (a) Majority spin channel and (b) minority spin channel.

tioned in a gap for one spin direction only. These materials are weak magnets by definition. Examples are Fe_3O_4,[7] $Fe_xCo_{1-x}S_2$,[8] and Mn_2 VAl.[9]

Category 1 is the only category where strong constraints on the crystal structure exist. This will be exemplified in this and the following paragraph. As an example NiMnSb is considered. Its band structure is shown in Fig. 1. It crystallizes in the Heusler $C1_b$ structure. Also another Heusler structure exists, the so-called $L2_1$ structure. In this structure the fourth position is also filled and compounds like Ni_2MnSb result, which is a normal ferromagnet. One could naively attribute the half-metallic properties of NiMnSb to its lower density with respect to Ni_2MnSb. In order to separate the influence of density and tetrahedral coordination, in Fig. 2 we show the band structure of Ni_2MnSb with a density equal to that of NiMnSb. It is clear that no half-metallic properties are present. Figure 3 shows the band structure of NiMnSb compressed to the density of Ni_2MnSb. The band gap has increased under compression, a rare (but not unique) phenomenon that also occurs in several group III–V semiconductors (because of the increased kinetic energy, the Fermi energy is positioned in the conduction band). It is important to notice that whereas half-metallic magnetism of the first category is impossible in the Heusler $L2_1$ structure, half-metallic magnetism of the other categories can still occur (e.g., the Heusler Mn_2 VAl belongs to the third category).

Finally, in order to show the importance of the minority *d* electrons, in Fig. 4 we show the band structure for NiMnSb with an artificially increased exchange splitting of the Hankel energies of the Mn *d* states. No half-metal is obtained, just like GaAs would not be semiconducting without Ga *p*

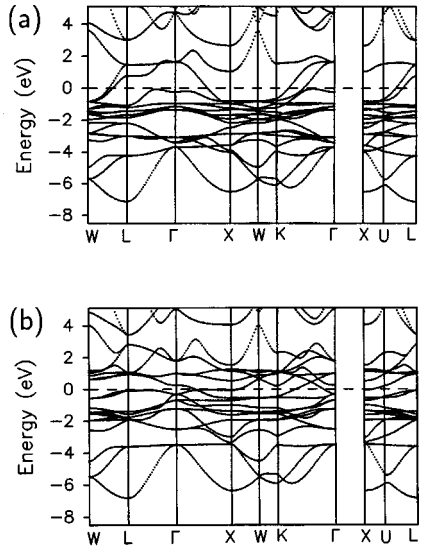

FIG. 2. Band structure of Ni_2MnSb at the density of NiMnSb. (a) Majority spin channel and (b) minority spin channel.

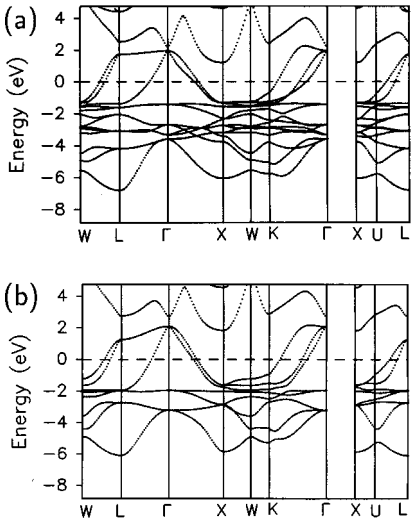

FIG. 4. Band structure of NiMnSb with an artificially increased exchange splitting. (a) Majority spin channel and (b) minority spin channel.

states. Half-metallic magnetism and strong magnetism are mutually exclusive for compounds in category (1).

II. SPIN POLARIZATION OF THE CONDUCTION

The degree of spin polarization in half-metals should be 100% at $T=0$, neglecting spin-orbit interactions. In the coming paragraphs we will consider the actual situation in several half-metals and try to rationalize the existing data. In this discussion it is important to be aware of the fact that several experimental methods actually measure the spin-polarization at the surface of the half-metal, or at an interface with some other medium. One has to keep in mind that a bulk electronic structure, a surface electronic structure, and the electronic structure at an interface can be very different.

The most straightforward case is CrO_2, where the half-metallic properties are generally accepted. It crystallizes in the rutile structure. This structure allows for a stoichiometric, hence electrically neutral, (001) surface, which is unlikely to reconstruct or to show surface segregation. Calculations show two oxygen-derived surface states in the band gap for the minority spin direction, but these states are located well below the Fermi energy and do not corrupt the half-metallic properties at the surface.[10] Experimentally CrO_2 shows the highest degree of spin polarization of all materials considered in Andreev reflection.[11]

The situation in the CMR and double perovskite materials is still the subject of active research. Band structure calculations show results which depend on the approximations involved. For example, for $La_{0.5}Ca_{0.5}MnO_3$ the local density approximation leads to a band structure where the Fermi energy just intersects the bottom of the minority t_{2g} band,[5,12] while a genuine half-metal is obtained in the generalized gradient approximation (GGA).[12] (Similar behavior is seen for Mn_2 VAl.[9]) Experimentally, for $La_{0.7}Sr_{0.3}MnO_3$ 78% spin polarization was measured with Andreev reflection,[11] while spin-resolved photo emission shows 100% polarization,[13] as expected for a half-metal. Unlike CrO_2, the cubic perovskite structure does not possess stoichiometric surfaces, so surface reconstructions and/or deviations from the ideal stoichiometry at the surface must occur. In this light it is possible that both surface-sensitive measurements show a different behavior, especially since one involves a surface and the other an interface. Moreover, no details of the interface structure or composition are available for the Andreev reflection experiment.

It is interesting to compare the situation with $LaSr_2Mn_2O_7$. This is the second member in the general perovskite series $A_{n+1}B_nO_{3n+1}$, the cubic one corresponding with $n=\infty$. This structure does allow for an electrically neutral (001) surface (assuming a plausible preference of the alkaline earth atoms for the surface layer). The calculated bulk and surface electronic structures are very similar indeed.[14] Unfortunately, this compound is not a genuine half-metal, even not in the GGA: The Fermi level touches the minority t_{2g} d band. Nevertheless, experiments on this compound should be stimulated, as will be clear from the next paragraph.

It is not obvious that the question whether the Fermi level intersects the minority t_{2g} band or not is relevant, since the majority e_g electrons are so much more mobile than possible t_{2g} minority electrons.[5] In this respect, the notion of a transport half-metal has been introduced.[15] This is an interesting concept, since it could be applied more generally: If the crystal field splitting and the widths of the bands derived from the crystal field levels originate from the same metal d–anion interactions—as is often the case—one expects the bandwidths to increase with energy systematically.[16] Given a large enough exchange splitting, the mobility of the minority electrons can be much less than that of the majority electrons. So this situation could occur in other, different situations as well. However, a degree of spin polarization as high as possible is required for some applications.[17]

The situation in NiMnSb is even more complex. Whereas measurements of the spin polarization in the bulk are consistent with a genuine half-metal (at least at low temperatures),[18,19] Andreev reflection shows a polarization of 58% only,[11] while spin-polarized tunneling gives an even lower (28%)[20] degree of spin polarization. Spin resolved photoemission shows polarizations that are very much dependent on preparation conditions, sometimes reaching 100% in the case of normal incidence inverse photoemission,[21] but not more than 40% in normal photoemission.[22]

It is well-known that disorder, especially Ni–Mn interchange, is detrimental for the half-metallic properties of NiMnSb.[23,24] Nevertheless, the explanation that disorder is responsible for the experimental observations is doubtful, since it contradicts the existing bulk measurements. Moreover, we calculated that a 3% Ni–Mn interchange costs 2.88 eV per Ni–Mn pair, an energy comparable with the heat of evaporation of the metallic constituents. Because Ni–Mn interchange is so effective in destroying the band gap, it is a very unstable configuration.

It is clear that deviations from the half-metallic behavior in NiMnSb are confined to the surface. Electronic structure calculations of several surfaces show that even without surface segregation no half-metallic surfaces are present. This situation is not unexpected. It results from the lack of the full crystal symmetry at the surface and is quite comparable with the situation in several group III—V semiconductors.[25]

The similarity between NiMnSb and zincblende semiconductors suggests that, while the surface of NiMnSb is not half-metallic, the interface with a zincblende semiconductor might be. A computational study was undertaken in order to investigate under which conditions half-metallic properties could be restored.[25] The study limited itself to CdS and InP, because they show a good lattice match with NiMnSb. In the (111) direction a perfectly half-metallic interface resulted (and in this direction only). The interface shows the existence of Sb–S pairs, just as in the insulating minerals gudmandite, costibite, and paracostibite.

III. A NEW HALF-METAL

One of the possible applications of half-metals is the injection of spin-polarized charge carriers into semiconduc-

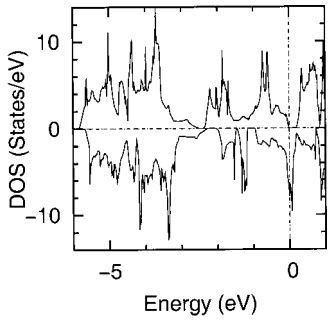

FIG. 5. Calculated GGA density of states of Li_3FeN_2. The Fermi level is at the zero of the energy scale. Majority and minority spin channels are plotted along the positive and negative ordinate, respectively. The calculation was carried out in a primitive cell, using tetrahedron integration (Ref. 31) and $7\times7\times7$ **k**-points mesh (Ref. 32).

tors. This was achieved successfully for electrons, employing magnetic semiconductors. These maintained their polarization over a long distance.[26] The situation for hole injection in conventional semiconductors like GaAs is much less favorable because of the depolarization induced by the spin-orbit splitting of the top of the valence band. This valence band top has primarily arsenic *p* wave function character. There is no orbit quenching to reduce the spin-orbit coupling at the $\mathbf{k}=0$ maximum.

In the longer term, it is inevitable that research will shift to semiconductors as light as possible in order to reduce the effects of the spin-orbit interaction, i.e., GaN or even AlN. Nitrides were, until recently, a rather underexposed class of materials, because of their complex synthesis. In order to investigate the possibilities of half-metallic systems, chemically compatible with nitride semiconductors, a search for half-metallic nitrides was started. As an example, the electronic structure of Li_3FeN_2 is reported here. Although its Curie temperature is low (10 K),[27] it may serve as an example. Li_3FeN_2 crystallizes in an orthorhombic cell with $a=4.872$ Å, $b=9.641$ Å, and $c=4.792$ Å.[27] The crystal structure shows edge sharing FeN_4 tetrahedra. The density of states was calculated for the experimental structure (Fig. 5). It was calculated with the Vienna *ab initio* simulation program.[28] For exchange and correction the GGA functional by Perdew *et al.* was employed.[29] The projector augmented wave method was used.[30] At low energies a complex of bands of primarily nitrogen *p* character is found. At higher energies a complex of Fe *d* states results, with a 0.2 eV band gap for the majority-spin direction. The moment is 1 μ_B/Fe atom, in agreement with experiment,[27] thus iron is in its low spin state here.

The observation of a low spin configuration here should not come as a surprise: The stability of a low spin vs a high spin configuration depends on the chemical surroundings of the transition metal. Where oxides in general have a tendency for a high spin configuration, this tendency is reduced in sulfides. Cynanides on the other hand invariably show a low spin configuration, while nitrides can show both. This ambivalence in the nitrides is another motivation for the study of their electronic structure. Spin electronics requires control over the spin direction of charge carriers injected into some device. The reversal of the direction of the spins of the charge-carriers is accomplished by the reversal of the direction of the magnetization by an applied field. But the reversal of the magnetization is a slow and noisy process. Nitrides are prime candidates for showing metamagnetic transitions, in other words the transition from a low to a high spin state by an applied magnetic field. Such an electronic transition is much faster than the reversal of the direction of the magnetization. If one of the two configurations is half-metallic, a useful switch would already emerge. Maybe metamagnetic materials exist where both the low and the high spin configuration are half-metallic, but with energy gaps for different spin directions. This would allow the reversal of the polarization of the conduction electrons without a reversal of the direction of the magnetization.

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