Spin-polarization in half-metals

Citation for published version (APA):

DOI:
10.1063/1.1452238

Document status and date:
Published: 01/01/2002

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:
• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher’s website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the “Taverne” license above, please follow below link for the End User Agreement:
www.tue.nl/taverne

Take down policy
If you believe that this document breaches copyright please contact us at:
openaccess@tue.nl
providing details and we will investigate your claim.

Download date: 10. Sep. 2019
Spin Polarization in Half-Metals

Vince Harris, Chairman

Spin-polarization in half-metals (invited)

C. M. Fang
Laboratory of Solid State and Materials Chemistry, Eindhoven University of Technology, P.O. Box 513, NL-5600 MB Eindhoven, The Netherlands

G. A. de Wijs and R. A. de Groot
Computational Materials Science, FOM Institute for Condensed Matter, Toernooiveld 1, NL-6525 ED Nijmegen, The Netherlands and Laboratory of Chemical Physics, Materials Science Center, Nijenborgh 4, NL-9747 AG Groningen, The Netherlands

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. © 2002 American Institute of Physics.

DOI: 10.1063/1.1452238

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 \( \sim 1 \) covalent band gaps, \( \sim 2 \) charge-transfer band gaps, and \( \sim 3 \) \( d-\)\( d \) 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 \( C1_3 \) structure, which is closely related with the zinblende structure: One of the empty positions is occupied by the third constituent (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 pseuoso-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., zinblende MnAs.\(^3\) However, the zinblende 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 \( \text{CrO}_2 \),\(^4\) 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-
tioned in a gap for one spin direction only. These materials are weak magnets by definition. Examples are Fe$_3$O$_4$, Fe$_x$Co$_{1-x}$S$_2$, and Mn$_2$VAl.

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$_2$MnSb result, which is a normal ferromagnet. One could naively attribute the half-metallic properties of NiMnSb to its lower density with respect to Ni$_2$MnSb. In order to separate the influence of density and tetrahedral coordination, in Fig. 2 we show the band structure of Ni$_2$MnSb 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$_2$MnSb. 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 $p$
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, metallic properties are generally accepted. It crystallizes in the highest degree of spin polarization of all materials considered in Andreev reflection. 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, while a genuine half-metal is obtained in the generalized gradient approximation (GGA). 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, while spin-resolved photo emission shows 100% polarization, 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$_2$Mn$_2$O$_7$. 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. 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. In this respect, the notion of a transport half-metal has been introduced. 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—such as is often the case—one expects the bandwidths to increase with energy systematically. 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.

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), Andreev reflection shows a polarization of 58% only, while spin-polarized tunneling gives an even lower (28%) 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, but not more than 40% in normal photoemission.

It is well-known that disorder, especially Ni–Mn intercalation to the surface. Bandstructure calculations of several surfaces show that even without surface segregation no half-metallic surfaces are present. The 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.

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. 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 gundmandite, 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-
tors. This was achieved successfully for electrons, employing magnetic semiconductors. These maintained their polarization over a long distance. 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 $k = 0$ 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$_3$FeN$_2$ is reported here. Although its Curie temperature is low (10 K), it may serve as an example. Li$_3$FeN$_2$ crystallizes in an orthorhombic cell with $a = 4.872$ Å, $b = 9.641$ Å, and $c = 4.792$ Å. 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. For exchange and correlation the GGA functional by Perdew et al. was employed. The projector augmented wave method was used. 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 $1 \mu_B$/Fe atom, in agreement with experiment, 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. Cyanides 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.

ACKNOWLEDGMENTS

This work is part of the research program of the Stichting voor Fundamenteel Onderzoek der Materie (FOM) with financial support from the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO).

2 A strong magnet is defined here as a magnet where a hypothetical increase in exchange splitting does not lead to an increase in moment. In practice this means that either the majority $d$ shell is full or the minority empty, e.g., nickel is a strong magnet, iron is a weak magnet.
16 This picture breaks down for crystal structures where the bandwidth is limited by another interaction, for example, the weak MnO$_3$–MnO$_3$ coupling in hexagonal YMoO$_3$ along the $c$ direction.
27 A. Guadat, R. Kniep, A. Rabenau, W. Bronger, and U. Rauschewitz, J.