Defects in half-metals and finite temperature

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Abstract
The influence of intrinsic defects in half-metals is calculated in the case of
NiMnSb. Of the 14 cases of intrinsic defects, five affect the half-metallic
properties. They are energetically very unlikely to occur. Circumstances are
discussed under which defects may even have a beneficial effect on the spin
polarization of the conduction electrons. *Non*-intrinsic defects, like deliberate
doping by rare-earth atoms, as well as the effect of nano-structured contacts may
influence the magnon spectrum, improving the behaviour at finite temperature.

1. Introduction

The role of intrinsic defects in half-metals has been studied for almost as long as half-metals
have been recognized. The original calculations on NiMnSb [1] were criticized for using a
crystal structure different from the one reported on the basis of neutron diffraction studies [2].
The latter crystal structure, which differs by the interchange of manganese and nickel atoms,
has no half-metallic properties. This prompted a neutron diffraction study in order to establish
the correct site occupancy as well as the degree of disorder. The crystal structure of [1] turned
out to be the correct one, no indication for site disorder was obtained and in particular the
(partial) interchange of nickel and manganese contradicts the magnetic properties [3]. In a
later computational study, Orgassa *et al* [4] showed that 3% of nickel–manganese interchange
destroys the half-metallic properties. Since this study appeared at the same time as experiments
showing a lack of half-metallic properties at the surface [5], it led to speculations about the
occurrence of disorder in NiMnSb. However, spin-resolved positron annihilation showed bulk
NiMnSb to possess a Fermi surface for one spin direction exclusively [6] to the precision

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of the experiment (0.01 electron). This is a very precise technique, not depending on ultra-low temperatures and high magnetic fields for its sensitivity. (Pockets of the Fermi surface can easily be overlooked by methods for the determination of the Fermi surface like De Haas–Van Alphen).

For various reasons a study of defects in half-metals seems timely, especially in view of the increasing number of studies on samples grown at low temperature out of thermodynamic equilibrium (MBE). Not only are the possible detrimental effects on the half-metallic properties of interest, but also the opposite effect should be investigated: can the deliberate introduction of defects enhance the spin polarization, especially at higher temperatures? The elementary magnetic excitations in a solid are the magnons. The magnonic band-structure shows magnon bands increasing in energy in going from the centre of the Brillouin zone towards the boundary. They describe the dispersion of the magnons. The Γ point represents a spin-spiral of infinite wavelength, while a k-point at the zone boundary (in a direction corresponding to a nearest neighbour direction in real space) describes an anti-ferromagnetic commensurate ordering in this direction. At finite temperatures these magnons can be excited, more easily for longer wavelength. This leads to a reduction of the spin polarization of the conduction electrons with temperature, until, at the Curie point, no net polarization will remain without an applied magnetic field. Usually, the use of half-metals as a source of spin-polarized electrons should be limited to temperatures well below the Curie temperature. In this regime an optimization of the polarization is possible by modifying the magnonic band-structure by suitable doping. Three strategies are investigated here. The first one is the introduction of impurities, that makes the half-metal amorphous, preferentially so for the magnons. An amorphous system shows discrete energy levels in contrast to the continuous bands in the crystalline state. Consequently, the number and type of magnons (a quite inappropriate name here) that can be thermally excited are different and consequently the temperature dependence of the spin polarization will also be different: better at some temperatures, worse at others. Of course, this strategy can only work if impurities can be found that affect the electronic structure as little as possible; in particular, the dopants should not affect the bandgap of the half-metal. The art is to design imperfections with an optimal magnonic, but a minimal electronic impact.

A second strategy is based on enhancing the magnetic anisotropy. The effect of the magnetic anisotropy is the introduction of bandgaps at the Γ point of the magnonic band-structure, since the energy depends on the direction of the magnetization through the magnetic anisotropy. The effect is to reduce the number of magnon states energetically available at a given temperature and thus reduce the temperature-induced depolarization of the conduction. This is beneficial at any temperature, but here also the important question is whether this can be achieved without degrading the half-metallic properties at even zero temperature.

The third possibility described here is the effect of replacing a macroscopic contact between the half-metal and some material wherein spin-polarized charge carriers are needed by a contact of many nano-sized half-metallic particles. Here also there is a serious complication: surfaces of half-metals are often not half-metallic, so, without special care, a nano-sized half-metallic particle will not be half-metallic for a non-negligible fraction of its volume [7].

All efforts along the lines sketched above will be useless unless dopants in half-metals can be found that maintain the half-metallic properties or a material can be designed to embed nano-sized half-metallic particles ensuring half-metallic interfaces. This preservation of half-metallic behaviour is the central subject of this paper. The examples worked out by means of electronic structure calculations are based on NiMnSb. The reason for this choice is that it has a high Curie temperature (740 K) and can be applied at low temperatures, unlike magnetite, which transforms into an insulator below 120 K. Also, it was recognized as a half-metal long ago and consequently has been studied in detail, both experimentally as well as computationally

and theoretically. Also, its crystal structure and chemical composition are quite similar to zinc-blende semiconductors. There are no reasons to assume, however, that a similar strategy could not work equally well for other half-metals.

First (in section 2), calculations on intrinsic defects are discussed. It is concluded that these are not suitable for improving finite temperature performance. In section 3 an example of a useful non-intrinsic defect is introduced. Section 4 combines the effort of section 3 with the enhancement of the magnetic anisotropy. Finally, in section 5, it is shown that a half-metallic nano-structured conctact can—in principle—be made, whence a promising strategy exists for spin-injection from quantum dots while preserving the half-metallic properties of these dots.

2. Influence of some (hypothetical) forms of intrinsic defects in NiMnSb

In order to understand the influence of various types of disorder on the electronic properties of NiMnSb, the structure and bonding in this compound are briefly discussed. NiMnSb crystallizes in the Heusler $C1_b$ structure, a face centred cubic structure which differs from the zinc-blende structure only by the presence of a third species at the $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ position. Nickel occupies the $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ position. The magnetic moment of 4 μ_B is carried by the manganese atom, hence the manganese atom for the minority spin is trivalent. This leads to a situation very similar to that in the III–V semiconductors: both the trivalent and the pentavalent (antimony) atoms occupy sites with tetrahedral coordination, while the nickel mediates the antimony–manganese interaction. Indeed, there is a strong similarity between the valence bands of GaSb and minority spin NiMnSb, especially if the occupied nickel d bands (but not their interactions) are removed [1]. This similarity reflects the near identical interatomic interactions in both cases. The tetrahedral coordination is as essential for the occurrence of a bandgap at the Fermi energy as it is for the III–V semiconductors. For the majority-spin direction all contributing basis states are degenerate in energy in a first approximation and consequently a band-structure results that is typical for an alloy: broad bands, three of which intersect the Fermi energy with a large slope. No bandgap exists for this spin direction.

The effect of disorder was investigated in a unit cell of 32 fu, so the concentration of defects is 3%. Most of the cases of disorder studied comprise the interchange of two species (where the empty $\frac{3}{4}, \frac{3}{4}, \frac{3}{4}$ site is considered as a species as well). The size of the unit cell allows two types of interchange for each case: interchanging nearest neighbours or interchanging more distant atoms. Both cases were investigated. As expected, the interchange of a nickel and a manganese atom destroys the half-metallic properties in both cases. The results for nickel–antimony interchange are somewhat surprising. Only in the case of interchanging more distant atoms are the half-metallic properties lost. The interchange of a nearest neighbour nickel–antimony pair preserves the half-metallic properties. Also, the case of manganese–antimony interchange is interesting. In the case of interchange of near atoms, the half-metallic properties are lost, but in the case of interchange of more distant atoms an occupied localized impurity state for the minority-spin direction shows up with the conservation of half-metallic properties. The displaced manganese atom shows a magnetic moment of 2 μ_B only. A similar behaviour is observed in displacing an antimony atom to an empty position, but with the results for the near and more distant interchanges reversed as compared with manganese–antimony interchange. The displacement of manganese atoms to empty sites does not affect the half-metallic properties, nor do the cases of nickel–empty site interchange. Finally, the presence of an extra nickel atom or a missing nickel atom does not destroy the half-metallic properties. So, the majority of the defects have no influence on the half-metallic properties, while the most damaging defect (nickel–manganese interchange) costs 2.88 eV, rendering its occurrence
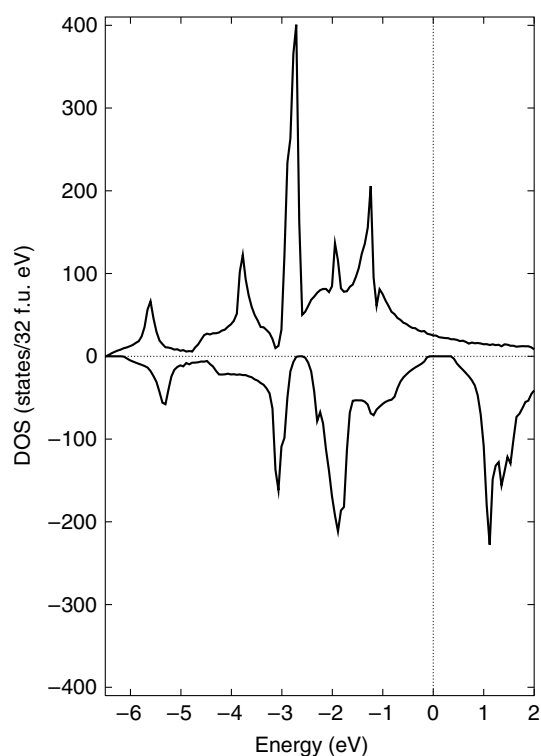
Figure 1. Density of states for the majority-spin direction and the minority-spin direction for NiMnSb with 3% Mn replaced by Sc. The Fermi level is at 0 eV.

highly unlikely. As mentioned before, the temperature dependence of the magnetization, neutron diffraction and positron annihilation did not show any indication of the presence of disorder. Moreover, early NMR work on NiMnSb showed the impossibility of the introduction of defects by even extensive cold working [8]. A recent NMR study on thin films of NiMnSb on GaAs (111) showed that even in samples prepared at low temperatures disorder was markedly absent [9].

3. Deliberate introduction of defects

Because of the difficulty of introducing intrinsic defects, discussed in the previous paragraph, the introduction of *non*-intrinsic defects in NiMnSb will be investigated in this paragraph with emphasis on the preservation of the half-metallic properties on one hand, while optimizing the magnetic disorder on the other hand. Since the magnetic moments are centred on the manganese atoms, the optimal impact can be expected by the partial substitution of non-magnetic atoms for the manganese. The preservation of the half-metallic properties requires in a first approximation the integrity of the bandgap. Since the origin of the bandgap is similar as in the III–V semiconductors, the non-magnetic atoms to replace the manganese should be preferably trivalent transition metals. Clearly scandium fulfils these requirement. Support for this idea is obtained from the fact that NiScSb actually exists and even crystallizes in exactly the same crystal structure as NiMnSb [10]. The calculated densities of states for NiMnSb with 3% of the manganese replaced by scandium are shown in figure 1. Clearly the half-metallic
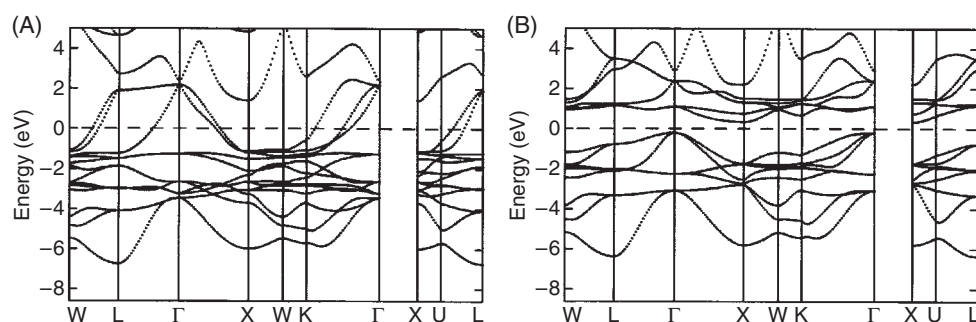
Figure 2. Band structure of NiMnSb for the majority-spin direction (A) and the minority-spin direction (B).

properties are completely conserved. The scandium sites show a negligible magnetic moment (less than 0.1 μ_B).

4. Enhancing the magnetic anisotropy

The origin of the magnetic anisotropy is mainly the spin–orbit interaction. The effect of this interaction in NiMnSb is expected to be weak. The strength of the spin–orbit interaction is an almost atomic quantity: it depends on the product of the wavefunction of interest and the gradients of the potential. The latter diverges at the nucleus, where the wavefunction vanishes; consequently, the spin–orbit interaction has its major contributions in areas rather close to the nucleus, not being influenced much by the chemical environment. The effect of the spin–orbit interaction of a given strength on quantities like the magnetic anisotropy and the spin mixing is greatly influenced by the band-structure, however. In a first order of approximation the spin–orbit interaction couples states with the same angular momentum l. It will do so independently of the occupation of these states, but net effects for the quantities we are interested in here only occur if the states are partially occupied. Also, in the first order, spin–orbit interaction couples states of the same k-vector only. This means that only those parts of the Brillouin zone that have partial occupation of the l manifold contribute. On top of this, there exists a competition between the band-structure and the spin–orbit interaction: chemical bonding opposes the spin–orbit coupling. This so-called orbital quenching is less effective, however, the higher the degeneracy of the l manifold. These rules can be summarized as follows. Given the strength of the spin–orbit interaction, its effect is optimal if states with high degeneracy are located close to the Fermi energy. This situation almost always occurs at a high symmetry point in the Brillouin zone. The flatness of the energy-bands here ensures the involvement of a larger part of the Brillouin zone, the (near) degeneracy in this part of the zone inhibits orbital quenching and the vicinity of the Fermi energy leads to partial occupation of the l manifold. Exactly the opposite situation is present in NiMnSb, where three non-degenerate bands with large slope intersect the Fermi energy in the middle of the Brillouin zone (figure 2).

Spin–orbit interaction causes the mixing of the two spin directions, leading to a reduction of the spin polarization of the conduction electrons even at zero temperature. Special care has to be taken to avoid the desired increase in the magnetic anisotropy being offset by this reduction. This latter effect takes place close to the Fermi energy, while the magnetic anisotropy can originate anywhere in energy as long as the l manifold responsible for it is only partially occupied. Ideally, this would imply a strong spin–orbit interaction in a core-like sub-shell.
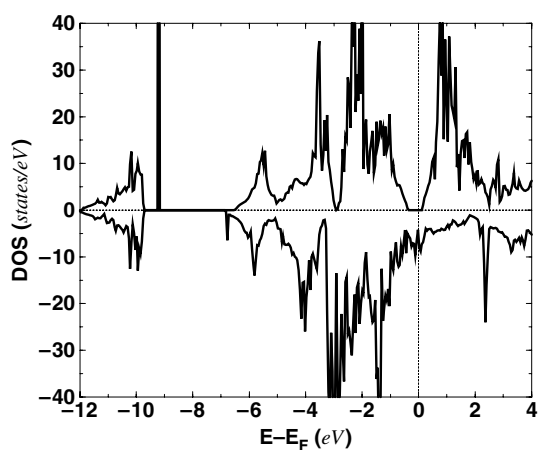
Figure 3. Density of states as a function of energy for holmium doped NiMnSb. The dashed line indicates the Fermi energy. Note the presentation of the bandgap for the minority-spin direction.

A properly chosen element from the lanthanide-series as a substituent could approximate this situation closely. The 4f electrons, not directly involved in chemical bonding, show a strong spin–orbit interaction and are energetically well separated from the Fermi energy. The choice of the lanthanide atom is determined by the requirement of both a spin moment (maximal halfway through the series) and an orbital moment (zero halfway through the series, optimal at one and three quarters of the way through the series). So holmium deserves serious consideration. The chance that this could be realized experimentally is indicated by the fact that NiHoSb does exist and actually is isostructural with NiMnSb [10]. From the point of view of the preservation of the half-metallic properties, the same line of reasoning as in the previous section can be extended to more rare earth elements as long as they are trivalent (europium and cerium have already been rejected based on their magnetic properties). Figure 3 shows the calculated density of states of NiMnSb with 13% of the manganese replaced by holmium. The half-metallic properties are completely conserved. The size of the effect is not determined by the strength of the spin–orbit coupling, but limited by the interaction between the magnetic moments of manganese and holmium (52 K). Consequently holmium performs best at low temperatures (liquid helium).

5. Embedding half-metallic quantum dots

The influence of finite size on the magnon spectrum is to replace the continuous spectrum by a discrete set of levels, not unlike the scenario for the substitution of scandium for manganese in NiMnSb. The advantage of considering a multitude of half-metallic quantum dots as a contact is that a direct control over the size of the energy gaps in the magnon spectrum is available through the size of the quantum dots. The surfaces of these quantum dots form a serious complication. In the case of NiMnSb, for example, it was shown that not a single low index surface shows half-metallic properties [7]. These calculations did allow for surface reconstructions within the size of the unit cell. Although no surface segregation was allowed in the calculations, it is more than likely that without a proper embedding in a suitable matrix an important fraction of the half-metal will not be half-metallic. A genuine half-metallic interface was obtained between NiMnSb and CdS [7]. But this result was obtained only for one specific
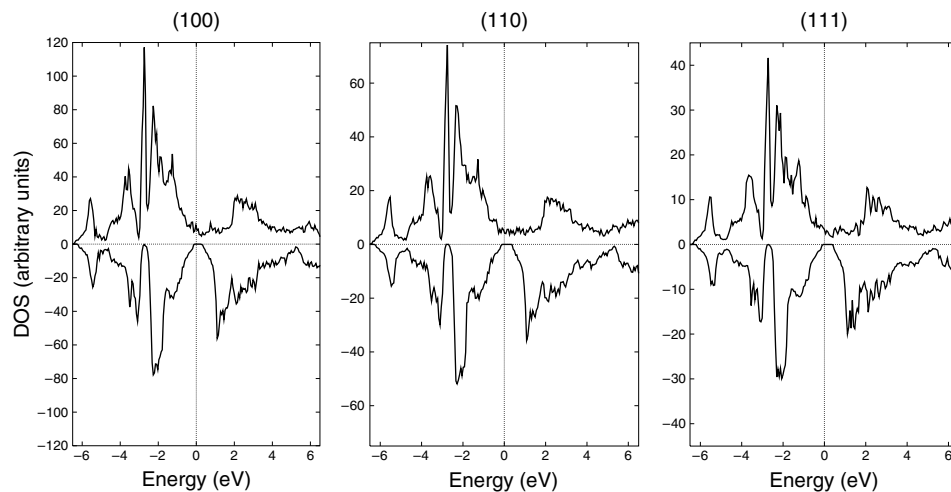
Figure 4. Density of states of the NiMnSb/NiScSb interface for the 100, 110 and 111 directions.

interface in one direction (111). The interface between the quantum dots and the embedding matrix will in general contain a multitude of orientations. On the other hand, the choice of the semiconductors (InP proved to yield half-metallic interfaces as well; these were the only cases investigated because of the lattice match) in [7] was motivated by the general interest in spin-polarized charge carriers in III–V semiconductors. No other requirements than just to restore half-metallic properties at the interfaces of as many orientations as possible exist for the embedding material. As mentioned before, NiScSb exists. It is a non-magnetic semiconductor with a calculated bandgap of 0.5 eV, so the actual bandgap could be of the order of twice this value. It is isostructural with NiMnSb and isoelectronic with the minority-spin direction of NiMnSb. Clearly this material is as closely related as possible to the minority-spin direction of NiMnSb and it is exactly the integrity of this aspect of the half-metal that we seek to achieve at the interface. Figure 4 shows the densities of states of the three interfaces of lowest index.

The temperature at which one desires to operate the contacts determines the optimal sizes of the bandgaps in the magnon spectra, which in their turn are defined by the sizes of the quantum dots. The distances between the dots also require consideration. Very short distances will lead to behaviour approaching that of a macroscopic contact; in the limit of large distances the Curie temperature will drop until even the super-paramagnetic regime may be entered.

Acknowledgments

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