Half-Metallic Antiferromagnets

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This Letter discusses the possibility of realizing half-metallic antiferromagnets, i.e., systems with 100% spin polarization of the conduction electrons without showing a net magnetization. The predictions are based on electronic structure calculations using the local density approximation.

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Half-metallic materials (HMM) are metallic for one spin direction while at the same time semiconducting for the other spin direction [1]. The predicted half-metallic properties of the archetype NiMnSb have been confirmed experimentally by the size of the magnetic moment, which is necessarily integral for a HMM (experimentally: $4.00\mu_B$) [2], the absence of a quadratic term in the temperature dependence of the resistivity [3] (since one magnon scattering is impossible in a half-metallic material at low temperatures), and directly by spin-resolved positron annihilation [4], which shows a Fermi surface for one spin direction only. Antiferromagnetism seems to exclude spin polarization of the conduction electrons. In a conventional antiferromagnet the vanishing of the net magnetic moment originates from a symmetry relation between sites of opposite spin or the occurrence of a spin-density wave. Either effect causes the electronic structure of the two spin directions to be identical, with, as a result, no polarization of the conduction electrons. In a half-metallic material another mechanism for the exact cancellation of the local magnetic moments is provided by the requirement of the net moment to be integral: for a carefully selected material this integer can be zero. Thus a complete spin polarization of the conduction electrons is not perse in contradiction with the notion of antiferromagnetism; the antiferromagnetism we are considering here is of a truly new nature.

Spin-polarized scanning tunneling spectroscopy (SPSTM) is of fundamental importance for obtaining spin-resolved information on an atomic scale. High density information storage and vertical recording trigger the interest in SPSTM from a technological point of view [5]. The focus on SPSTM has revived the interest in half-metallic magnetic materials. A complication in SPSTM is the presence of a permanent magnetic tip a couple of angstroms away from the (magnetic) surface one seeks to investigate. Ideally one would like to apply a half-metallic antiferromagnet here.

The purpose of this Letter is to describe two such materials—one multilayer system and one bulk material—which may have a good chance of being realized experimentally. In all calculations reported in this Letter the localized spherical wave method was used [6].

The strategy is best illustrated by substituting Ni in NiMnSb by elements to the left of it in the three-dimensional (3D) series of the periodic table. CoMnSb in the Heusler $C1_b$ structure is calculated to be half metallic [7], with a moment of $3\mu_B$. FeMnSb is an interesting case [8]: it is half metallic with a net moment of $2\mu_B$ and local moments of Fe and Mn of $1\mu_B$ and $3\mu_B$, respectively, i.e., it introduces the notion of antiferromagnetic coupling in order to maintain the energy gain of the gap. MnMnSb is ferrimagnetic with $1\mu_B$ while CrMnSb [9] is calculated to be a half-metallic antiferromagnet. Thus, the electronic structure for these four materials combines an isoelectronic behavior for the semiconducting spin direction with the reduction of the number of valence electrons replacing Ni by atoms to the left of it in the 3D series completely accommodated for by the metallic spin direction.

Unfortunately the experimental reality is not so simple. CoMnSb forms actually a deformed superstructure and is not half metallic, FeMnSb cannot be prepared with the required stoichiometry [8], Mn_2Sb and CrMnSb [10] do exist, but crystallize in the Cu_2Sb structure and are calculated to be normal metals. It should be mentioned, however, that the Heusler $C1_b$ structure viewed along the (111) direction consists of hexagonal layers of its constituents, and recently the existing half-metallic ferromagnet PtMnSb could also be prepared in a molecular beam epitaxy (MBE) experiment which avoids the constraints of thermodynamic equilibrium [11]. MBE experiments on CrMnSb look extremely desirable.

Since the outcome of the MBE experiments is unclear, we focus here on the possibility of realizing a stable bulk antiferromagnetic half-metallic system. There exists a material which is isoelectronic with CrMnSb and does crystallize in the Heusler $C1_b$ structure: VFeSb [12,13] (the importance of the crystal structure for half-metallic properties was explained in Ref. [1]). Its density of states is shown in Fig. 1. It is a nonmagnetic semiconductor. Clearly the energy gain of a gap for the second spin direction exceeds the exchange energy of a (half-metallic) magnetic solution in the case of VFeSb. Since the lower coordination at the surface may enhance the tendency towards magnetism, the surface electronic structure was also calculated using the slab geometry, but VFeSb remains

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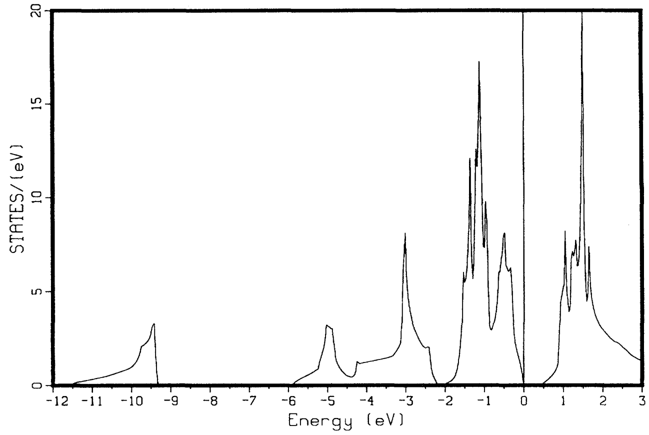

FIG. 1. Density of states of VFeSb.

semiconducting and nonmagnetic in our calculations up to the surface. Consequently a series of calculations was performed using the virtual crystal approximation in order to investigate how much the nuclear charge of vanadium has to increase to find a transition towards a magnetic solution. In order to maintain isoelectronicity we reduced the nuclear charge of Sb by the same amount. The transition was found to occur below 1/4 of an elementary charge. This situation is realized by considering substitutions for V and Sb by existing atoms, V by Mn and Sb by In. The reason we do not consider Cr and Sn is that MnFeIn exists in the related $\mathrm{InNi_2}$ structure, whereas to the best of our knowledge CrFeSn does not exist (at least, has not been described in the literature).

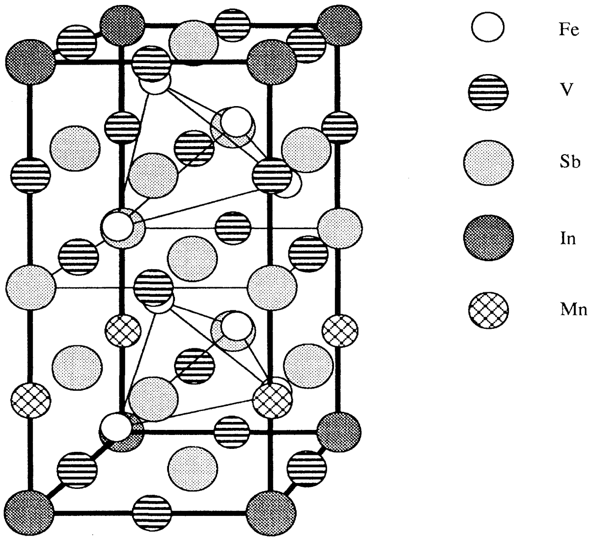

FIG. 2. Unit cell of the configuration of $\mathrm{V_7MnFe_8Sb_7In}$ with the lowest total energy.

Five supercells were considered, two with 25% substitution (overall stoichiometry of the unit cell $\mathrm{V_3MnFe_4Sb_3In}$) and three with $12\frac{1}{2}\%$ substitution ($\mathrm{V_7MnFe_8Sb_7In}$). The two cases with 25% substitution differ in the In-Mn distances which were closest together (2.926 Å) or further apart (5.067 Å). The systems of $12\frac{1}{2}\%$ substitution had the same two In-Mn distances, but this larger cell allows the In-Mn pairs for the smaller distance to be isolated or to form In-Mn-In chains, as in the 25% case, leading to three possibilities. The system with $12\frac{1}{2}\%$ substitution and In-Mn-In chains was nonmagnetic and metallic. All other supercells considered were half-metallic antiferromagnets with fairly constant local magnetic moments around $2.3\mu_B$/Mn atom and an energy gap of 0.35 eV. In all half-metallic cases, the Fermi level was positioned at the top of the valence band of the semiconducting spin direction. The lowest total energy of the three cases with $12\frac{1}{2}\%$ substitution is the case with "isolated" Mn-In pairs. This unit cell is shown in Fig. 2, while the calculated density of states curves for this configuration are shown in Fig. 3.

In summary, electronic structure calculations show that substituting $12\frac{1}{2}\%$ of V by Mn and Sb by In in existing VFeSb leads to a half-metallic antiferromagnetic system, i.e., a system with 100% spin polarization of the conduction electrons and no net magnetic moment. This system looks very promising as a tip material in spin-polarized STM, especially while the positioning of the Fermi level at the top of the valence band allows switching from a spin-polarized to a non-spin-polarized mode by reversing the polarity of the bias voltage.

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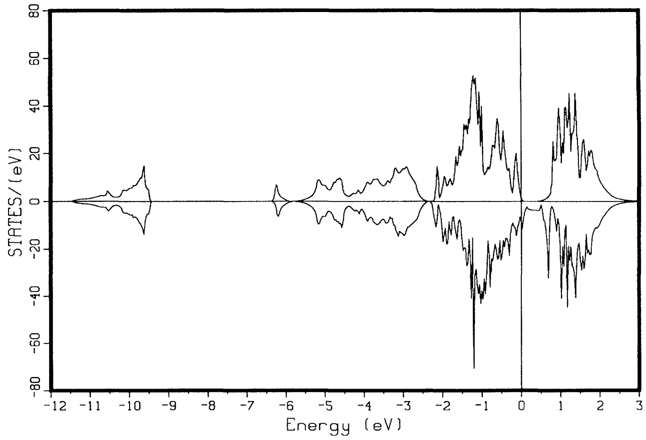

FIG. 3. Density of states of the configuration of $\mathrm{V_7MnFe_8Sb_7In}$ with the lowest total energy.

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