New Class of Materials: Half-Metallic Ferromagnets

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The band structure of Mn-based Heusler alloys of the $C1_b$ crystal structure (MgAgAs type) has been calculated with the augmented-spherical-wave method. Some of these magnetic compounds show unusual electronic properties. The majority-spin electrons are metallic, whereas the minority-spin electrons are semiconducting.

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Magnetic materials based on the $L2_1$ and $C1_b$ crystallographic phases have been of interest to both theorists and experimentalists since they were first considered by Heusler.[1] His interest focused on the unusual result that some of these materials in these crystallographic phases were strongly ferromagnetic but were made by combining elements which at the time were considered to be nonmagnetic. Subsequently these materials have been used as both a testing ground for theoretical models and also for the development of new magnetic systems. In this Letter we will show that some of these $C1_b$ type compounds encompass a new class of materials. The members of the novel class share simultaneously the property of an energy gap between valence and conduction bands for electrons of one spin polarization and the property of continuous bands for the electrons of the other spin polarization. This asymmetric band character reflects the character of the $C1_b$ structure itself: The minority-spin electrons are semiconducting while the majority-spin electrons keep their normal metallic character. As a consequence we have the remarkable situation here that the conduction electrons at the Fermi level are 100% spin polarized. This property may exist for *some* of the conduction electrons in other ferromagnets, for example, for the *d* electrons of Ni or the V electrons of VPd_3.[2] But in the present materials the unusual situation exists that the spin polarization entails *all* of the conduction electrons.

NiMnSb crystallizes in the $C1_b$ structure (MgAgAs type) which is face-centered cubic (fcc), space group $F43m$ (number 216 in the International Tables).[3] This structure type is often observed for ternary transition-metal intermetallic compounds (XYZ) and is closely related to the ordinary $L2_1$ Heusler alloys (X_2YZ). Both structure types can be described by means of four interpenetrating fcc lattices. For the ordinary $L2_1$ Heusler alloys these fcc lattices can be characterized by the positions X_1 $(\frac{1}{4}\frac{1}{4}\frac{1}{4})$, X_2 $(\frac{3}{4}\frac{3}{4}\frac{3}{4})$, Y $(0\,0\,0)$, and Z $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$. The same holds for the $C1_b$ structure with the exception that the X_1 positions are empty. The nearest-neighbor coordination of the X_2 atoms is similar in the two types of Heusler alloys X_2YZ and XYZ. This coordination consists of two interpenetrating tetrahedrons, involving four Y atoms and four Z atoms, respectively. The coordination of the Mn atoms is distinct, though, in both types of materials. As a consequence of the X_1 sites being empty in XYZ, the point symmetry of the Mn sites has been modified from O_h in the $L2_1$ type to T_d in the $C1_b$ type. The importance of this broken inversion symmetry will be discussed below.

For the calculation we have used the augmented-spherical-wave method of Williams, Kübler, and Gelatt.[4] Scalar relativistic effects were included as described by Methfessel and Kübler.[5] The empty X_1 sites were treated as atoms with zero nuclear charge. The basis included *s*, *p*, and *d* functions for all sites. The secular matrix was complex of rank 36. The internal summations in the three-center contributions to the matrix element were carried out including $l = 3$ contributions.[4] The bands converged on a better than 1 mRy scale. The experimental lattice constants were used.[3] Self-consistency was achieved in 12 iterations to a precision of 1:10.[5] Figures 1(a) and 1(b) show the band structure of NiMnSb in the majority- and minority-spin directions, respectively. A striking feature is that the minority band structure has a semiconducting gap straddling the Fermi level, whereas the majority band structure has metallic intersections.

There are three main elements and their inter-

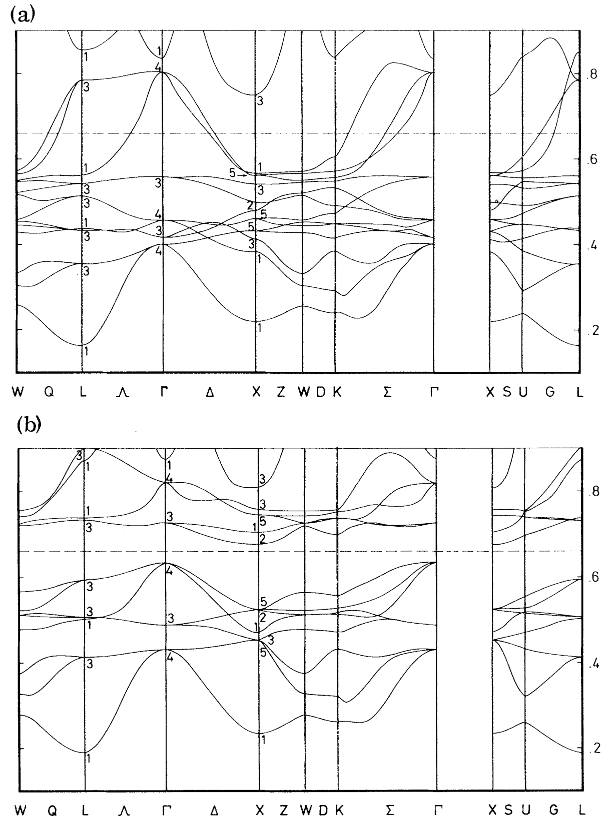

FIG. 1. Band structure of NiMnSb for (a) the majority-spin direction and (b) the minority-spin direction. A band at low energies (<0.2 Ry) of mainly Sb-s character has been omitted. The symmetry labels are those according to Ref. 6.

play which are responsible for the peculiarities of half-metallic ferromagnets: the crystal structure; the valence-electron count, and covalent bonding; and the large exchange splitting of the Mn $3d$-electron band states.

We begin by considering the majority band structure (metallic), Fig. 1(a) alone. *A priori* it does not seem particularly unusual or novel that a ferromagnetic Heusler alloy would have conduction electrons near the Fermi level.[4] Moreover, this is also the normal situation in Ni metal itself. Looking at this spin polarization alone one would hardly think that anything novel had occurred.

We now turn to Fig. 1(b), the minority band structure alone. Again we see something quite usual—a material with an energy gap straddling the Fermi energy, somewhat similar to GaSb. In addition, the flatness of some of the band structure implies that d electrons are playing a dominant role. But many magnetic semiconductors already exist so that one would hardly think that anything novel had occurred. The novelty is that the bands given in Figs. 1(a) and 1(b) are *both* present in the *same* material at the *same* time. This leads to 100% spin polarization of the conduction electrons. Now, since NiMnSb is a ternary compound, the total band structure in Fig. 1 is complicated. Nevertheless, the essential features for the different band structures in Figs. 1(a) and 1(b) themselves are rather simple and straightforward. We concentrate first on communality. Most of the structure below 0.5 Ry is topologically identical, reflecting a common origin of the bonding. For simplicity we consider only the lowest Γ_3 and Γ_4 levels, and their associated bands. These are dominantly formed from weakly spin-polarized Ni d states comprising the ϵ_g and t_{2g} symmetry levels, respectively. The Ni atoms and their d electrons are barely important in the half-metallic metals. The corresponding bands are far away from the Fermi level and are "neutral," i.e., they are the same for electrons of both spin polarizations. In a similar way the dispersion relations of states far *above* the Fermi level, and off the panel of the figures, are also "neutral." What is dominantly different in the two figures is—of course —the position of the Mn d electrons, which here, as in all Heulser alloys, are strongly spin polarized themselves. Why then does one have the peculiar feature here in these half-metallic ferromagnets? As is well known, the $L2_1$-type Heusler alloys have normal metallic behavior for both spin polarizations.[4]

A detailed comparison of $L2_1$ type Heusler alloys and the present $C1_b$ compounds shows *more* similarities than differences. Both classes of materials show large Mn d-electron exchange splittings, and the resultant Mn d bands tend to be polarized away from the Fermi level. The dominant difference between the normal Heusler alloys and the half-metallic ferromagnets is the *loss* of inversion symmetry in that the Mn sites in normal Heusler alloys have O_h symmetry whereas here they have only T_d. The consequence of this broken symmetry is that not only has time-reversal symmetry been broken—as in every ferromagnet—but with the breaking of inversion symmetry, *conjugation* symmetry is broken, too. The upshot is that conjugation or spin flip is distinct in the two classes. Concomitantly the coupling of states or bonding of electrons is also drastically altered. The result of this modified point-group symmetry is that the distinction between the t_{2g} d and p character of the electrons is

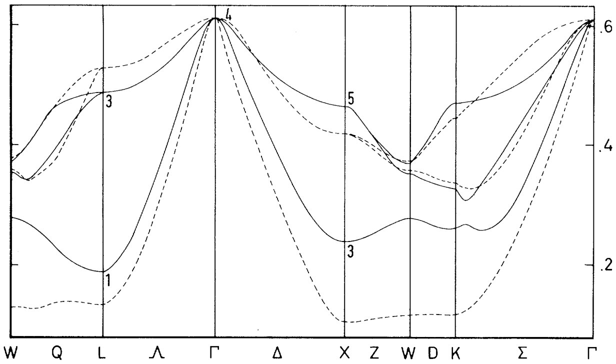

FIG. 2. Valence-band structure of minority-spin (semiconducting) NiMnSb ($C1_b$ structure) where the Ni-d states were deliberately removed from the Hamiltonian (full lines). For comparison the valence-band structure of GaSb (calculated with the same method) is shown (broken lines).

lost. The Sb p electrons now bind the Mn t_{2g} electrons in a very different way compared to the normal Heusler alloys. In the majority-band case the interaction of these Γ_4 levels leads to a mutual repulsion so that the Sb p states are pushed to energies above the Fermi level. These Γ_4 levels of primarily Sb-p character connect with lower states and are responsible for the metallic character of the majority-band structure. Since the Mn d levels are polarized above the Fermi level in the minority-spin direction, the same interaction of Sb p and Mn t_{2g} states presses the Sb p levels below the Fermi level, opens a gap, and produces semiconducting behavior. The Mn Γ_3 levels of e_g symmetry do not interact with the Sb p states and show normal spin polarization: they are located below and above E_F for the majority- and minority-spin directions, respectively. Interestingly enough, the bands of the minority-spin direction bear a striking resemblance to those in GaSb, obscurred because of the Ni d bands. In order to test this idea we have made a separate set of calculations based on the $C1_b$ structure, deliberately removing the d states of Ni. The resultant valence-band structure is shown in Fig. 2 as the full lines. Superimposed we show the electronic structure of GaSb as the dashed lines. The bands are rather similar, but the wave-function character is different on the Mn and the Ga sites, the covalently bonded p states of Ga being replaced by the t_{2g} states of Mn. Thus the exchange interaction of the Mn d electrons split above and below the Fermi level, when combined with the intrinsic covalently bonded Sb p states, produce the metal-semiconductor asymmetry observed in the electronic structure of NiMnSb.

A number of experiments have already been carried out for materials in this class of $C1_b$-type compound (magneto-optic properties, magnetic properties, NMR, and Mössbauer-effect data; see for instance Campbell[7] and Endo[8]). We briefly consider here some of the magnetic properties, and will discuss more properties in an extended paper later. The comparison of the results of the magnetic moments of the several $C1_b$ compounds we list in Table I is similar to that given by Williams, Kübler, and Sommers for $L2_1$ Heusler alloys.[10] The calculated magnetic moments follow closely the experimental values and trends. We conclude from our work and also from that of Williams, Kübler, and Sommers[10] that an itinerant-electron band model within the local-density formalism is an accurate way to describe the magnetic properties of Heusler materials.

The existence of a gap in the minority-spin bands is a striking feature of these materials. We now discuss those effects and interactions left out of our present work and considerations which might obviate this feature. We have not included in the work presented in Fig. 1 the effect of spin-orbit coupling. The Γ_4 state at the top of

TABLE I. Density of states at the Fermi level $N(E_F)$ (in states/Ry cell spin) and (Mn) $3d$ electron count n_{3d} calculated for the majority band (↑) and minority band (↓), respectively. In the last two columns the calculated total moments are compared with the corresponding experimental values (from Ref. 9).

Compound	$N(E)\uparrow$	$N(E)\downarrow$	$n_{3d}{}^{\mathrm{Mn}}\uparrow$	$n_{3d}{}^{\mathrm{Mn}}\downarrow$	$\mu_{\mathrm{tot}}{}^{\mathrm{cacl}}$	$\mu_{\mathrm{tot}}{}^{\mathrm{exp}}$
NiMnSb	9.90	0	4.51	0.87	4.00	3.85
PtMnSb	10.05	0	4.57	0.79	4.00	3.97
PdMnSb	9.04	2.97	4.58	0.71	4.05	3.95
PtMnSn	9.78	19.31	4.40	0.78	3.60	3.42

the valence band in the minority-spin direction will split under the influence of spin-orbit interaction into three sublevels. Estimating the spin-orbit splitting from the atomic values[11] we find that NiMnSb will remain a semiconductor in the minority-spin direction, while in PtMnSb the split-off singlet band will cross the Fermi level. Band methods similar to the augmented-spherical-wave method have been utilized in calculating gaps in several semiconducting or covalently bonded systems.[12,13] These calculations consistently found gaps 30% *smaller* than those found experimentally. We conclude that if the present results are inaccurate, the *existence* of a gap in the minority band is not in doubt.

The asymmetry of the minority and majority electronic structure which we have presented in Fig. 1 should lead to a number of unusual magnetically based physical properties. PtMnSb has recently been found to be the material with the highest magneto-optical Kerr rotation at room temperature.[9] Many effects based on a 100% conduction-electron-spin polarization can be measured and should result in unusual phononic, magnonic, spin-fluctuation, tunneling, and point-contact spectroscopy effects.

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