I. INTRODUCTION

The cubic Heusler structure class $X_2YZ$ of intermetallic compounds provides a great variety of behavior, including an interesting variety of magnetic phenomena. A striking example is the prediction, solely from band theory, of half-metallic (HM) ferromagnetism (FM) in this class (and the related half-Heuslers XYZ).

In the Heusler systems HM FM has never been unambiguously confirmed by experiment, although there is strong evidence in some cases. Only in the “colossal magnetoresistance” system $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ have HM signatures been seen directly and clearly in spin-polarized photoemission experiments, as was predicted from band theory calculations utilizing the local density approximation (LDA) for the exchange-correlation energy functional. Probably several Heusler and half-Heusler compounds are HM.

Over the past fifteen years many (probably at least twenty) HM FM compounds have been predicted based on LDA, and there has not been much reason to doubt the computational results (for example, these are not strongly correlated materials). Recent examples include $\text{Sr}_2\text{FeMoO}_6$, which appears to be supported by experimental data, and possible HM materials with vanishing moment – “HM antiferromagnets” – which have not yet been made. However, there is a need to make predictions as robust as possible, and in the double perovskite structure of $\text{Sr}_2\text{FeMoO}_6$ and the proposed HM antiferromagnets structural distortions are a likely occurrence and cloud the forecasts based on an ideal structure. The Heusler structure we consider here are much less inclined to distortion, leaving the prediction based solely on the quality of the electronic structure description.

Here we present a case of a Heusler structure compound where the use of the generalized gradient approximation (GGA) to the exchange-correlation energy functional leads to the prediction of a qualitatively different type of behavior compared to LDA. GGA has a stronger formal foundation, because it accounts specifically for density gradients that are neglected in LDA, and does so in a way that satisfies several exact constraints on the form of the exchange-correlation energy functional. Put into practice, GGA seems to give a general improvement in comparison to experimental data for alkali metals, $3d$ and $4d$ transition metals, lanthanides, and ionic insulators. For covalent semiconductors the reports are somewhat inconclusive, but overall GGA seems to be roughly as good as LDA. Assessing the differences between GGA and LDA is delicate, requiring in principle a full potential method. Because the GGA potential requires a more demanding calculation than does LDA, there are not yet many tests for multicomponent intermetallic compounds.

The compound in question here is the Heusler compound $\text{Mn}_2\text{VAI}$. This compound is somewhat peculiar regardless of its detailed electronic structure: whereas there are many Heusler compounds of the form $X_2YZ$ where $Y=\text{Mn}$, this compound is the only one reported where the $X$ site is occupied by Mn. In the $Y$ site Mn has high spin (around 4 $\mu_B$ in $\text{X}_2\text{MnZ}$ compounds), while in the $X$ site in $\text{Mn}_2\text{VAI}$ it has been found in LDA calculations that it has a low spin, in agreement with measurements. Although V and Al atoms may substitute on each other’s sublattice, in the system $\text{Mn}_2\text{V}_{1+x}\text{Al}_{1-x}$ the lattice constant and xray intensities show a kink at $x=0$, clearly identifying the stoichiometric composition. The structure remains the Heusler one from $x$ between -0.3 and +0.2, with linearly varying saturation moment. At stoichiometry the saturation moment is reported to be 1.9 $\mu_B$, close to the integral value characteristic of the spin moment of HM magnets, and the Curie temperature is $T_C = 760$ K. The Curie constant obtained from high temperature susceptibility (above $T_C$) is consistent with the saturation moment. Nakamichi and Stager inferred from NMR spin echo data that Mn and...
V have moments near 1.2 and -0.7 \( \mu_B \) respectively, making the net value (2\times 1.2 - 0.7) roughly consistent with the reported saturation magnetization. Itoh et al. \[17\] obtained from neutron diffraction 1.5\pm 0.3 and -0.9 \( \mu_B \) for Fe and V respectively.

Another reason for interest in this compound is the recent excitement caused by the related isostructural compound Fe\(_2\)VAI. From heat capacity, resistivity, and photoemission data this compound appears to be ‘chubby fermion’ metal, while LDA (and GGA) calculations \[18–20\] indicate that it has a semimetallic band structure with a very small number of carriers. One likely scenario is that its effective mass is enhanced by dynamic electron-hole correlations. \[20\]

In this paper we provide the results of accurate GGA calculations for Mn\(_2\)VAI. LDA calculations were presented earlier by Ishida, Asano, and Ishida \[21\], who obtained a near-HM situation that is reproduced by our LDA calculations. The important feature is that GGA predicts a HM FM (actually, ferrimagnetic, due to the moment of V that opposes the Mn moments). Recently there is increasing evidence that very large magnetoresistance and half-metallicity are closely related, for example in the ‘colossal magnetoresistance’ manganites \[2\] and in the double perovskite compound Sr\(_2\)MoRuO\(_6\). \[4\] Due to this apparent close connection between HM behavior and large magnetoresistance, our predictions suggest that the magnetoresistance of Mn\(_2\)VAI should be measured. In Sec. II we describe the structure and outline our method of calculation. The results and comparison with Fe\(_2\)VAI are given in Sec. III. The conclusions are summarized in Sec. IV.

II. HEUSLER STRUCTURE, AND METHOD OF CALCULATION

Although the Heusler structural class includes an alloy system where the atoms on the Y and Z sites often intermix, indications are that at stoichiometry this compound corresponds to an ideal Heusler (L2\(_1\)) structure compound. This structure type, pictured in Fig. 1, is based on an underlying bcc arrangement of atomic sites with lattice constant \( a/2 \), with V at (0,0,0), Al at \((\frac{1}{2}, \frac{1}{2}, \frac{1}{2})a\), and Mn atoms at \((\frac{1}{4}, \frac{1}{4}, \frac{1}{4})a\) and \((\frac{3}{4}, \frac{3}{4}, \frac{3}{4})a\), where \( a=5.875 \) \( \AA \) is the lattice constant of the resulting fcc compound.

This structure is also that of Fe\(_2\)VAI and of Fe\(_3\)Al, the latter of which has two inequivalent Fe sites (X and Y sites). There is no report that Mn\(_3\)Al forms in this structure.

We have applied the linearized augmented plane wave method \[22\] that utilizes a fully general shape of density and potential. The WIEN97 code \[23\] has been used in the calculations. The lattice constant of 5.875 \( \AA \) was used. LAPW sphere radii \( R \) of 2.00 a.u. were chosen with cutoffs of \( RK_{\text{max}} \) up to 8.7, providing well converged basis sets with more than 500 functions per primitive cell. Self-consistency was carried out on k-points meshes of around 200 points in the irreducible Brillouin zone \((12\times12\times12 \text{ and } 20\times20\times20 \text{ meshes})\). The GGA exchange-correlation functional of Perdew et al. \[7\] was used in the present work.

III. DISCUSSION OF RESULTS

A. Ferrimagnetic Mn\(_2\)VAI

The majority and minority (which we will refer to as up and down) band structure resulting from GGA are shown in Fig. 2. These band structures are similar to what is obtained using LDA (see Ishida et al. \[21\]) except for the important difference that the gap in the majority bands at the Fermi level \( E_F \) is increased by 40\% (from 0.25 eV to 0.35 eV). The position of \( E_F \) is essentially pinned by the minority band filling, and there is not any comparable band shifts in the minority bands within a few tenths of eV of \( E_F \). The result of GGA, arising from the increase in the gap and the associated band rearrangements, is to empty the valence holes in the majority bands. The net (spin) magnetic moment is exactly 2 \( \mu_B \) per unit cell. The magnetic alignment is ferrimagnetic, with roughly a moment of 1.5 \( \mu_B \) on each Mn and -0.9 \( \mu_B \) on V (see below for more discussion).
A very noticeable occurrence is just how different the majority and minority bands, shown in Fig. 2, are within 1 eV of $E_F$. In the majority bands the direct bandgap of 0.36 eV occurs at $\Gamma$; in the minority bands the nearest bands to $E_F$ are 1 eV away at $\Gamma$, both higher and lower. This difference, which is a drastic departure from simple Stoner exchange splitting, is related to ferrimagnetism, for which the exchange potentials are of opposite signs on the Mn and V atoms.

The atom and symmetry projected densities of states (PDOS) shown in Fig. 3 clarify the characters of the bands. The spin up bands below the gap are $\approx80\%$ Mn, including all of the majority Mn $t_{2g}$ states. Hence the Mn moment is strongly $t_{2g}$ in character. Since for V only $t_{2g}$ states are occupied in either spin channel, the V moment is also $t_{2g}$ in character. The Al character is so small as to be difficult to see on the scale of Fig. 3, so it is not shown.

Above the gap lies most of the V spin up states, along with much of the Mn $e_g$ states. In the spin down states below 0.5 eV, there are roughly equal amounts of V ($t_{2g}$) and Mn (mixed) states. Around $E_F$, however, the DOS is overwhelmingly Mn (strongly $t_{2g}$) in character. Hence the (100% polarized) charge carriers are associated almost entirely with Mn atoms.

The mechanism for antiparallel alignment of the V and Mn spins is not evident from our calculations. When parallel moments on V and Mn are used to begin the calculation, the V spin flips direction. This behavior suggest the FM alignment is substantially above the ferrimagnetic one in energy. Although it is tempting to speculate that the opening of the gap in the majority channel lowers the energy, which would provide a specific driving force toward half-metallicity, there is no particular evidence from our calculations to support such a scenario.

### B. Fermi Surface

With the exception of positron annihilation studies of the half-Heusler compound NiMnSb, Fermi surfaces of half metallic ferromagnets have not been directly measured, so we provide a brief description of the Fermi surface. The Fermi surface, which is of course solely for the minority bands, is rather interesting. It consists of small X-centered electron ellipsoids (nearly spherical) containing electrons, a large “jungle gym” type surface with arms along the cubic axes (Fig. 4), and a highly multiply-connected sheet that might be considered as centered at the L point of the Brillouin zone (Fig. 5). From Fig. 2, it can be seen that there is a near degeneracy of three bands (within 12 meV) that fall almost exactly at (actually straddle) the Fermi level.
FIG. 4. Fermi surface of the lower band, which is of the general “jungle gym” type centered at Γ. There is also a tiny spheroid centered at the X points. The shading reflects the carrier velocity, which is smallest along the (111) directions and largest along the (110) direction.

FIG. 5. Fermi surface of the higher band, with the cubic axes provided for orientation. This surface is multiply connected, with the L point (center of the hexagonal face) lying at the center of the portion that is shown (in one octant of the zone). The narrow neck at the L point is very sensitive to the Fermi level position.

This coincidence leads to identifiable structure in both Fermi surfaces. The jungle gym sheet has protrusions along the (111) direction very near the L point, while the surface in Fig. 5 has a narrow neck at the L point. The jungle gym also has flat regions perpendicular to the (110) directions that provide a nesting wavevector at $(0.85,0.85,0)\pi/a$ and symmetry related wavevectors. The surface in Fig. 5 has some flattish regions but no obvious strong nesting features.

C. Comparison with Fe$_2$VAI

Both from experiment and from the band structure, Fe$_2$VAI is vastly different from Mn$_2$VAI in spite of its identical structure and closely related constituents. The total and projected DOS of Fe$_2$VAI is shown in Fig. 4 for comparison with Mn$_2$VAI. Fe$_2$VAI is a semimetal, practically a semiconductor, with a very deep and 1 eV wide pseudogap centered on the Fermi level. In fact, the majority bands of Mn$_2$VAI, which are isoelectronic with the majority bands of Fe$_2$VAI, have rather similar projected DOS, with the 1 eV pseudogap in Fe$_2$VAI becoming a 1.5 eV pseudogap with a true gap in the center for Mn$_2$VAI. The pseudogap in Fe$_2$VAI no doubt plays an important role in stabilizing the non-magnetic state in that compound.

In the minority channel the electronic structures of the two compounds are quite distinct. Where in Fe$_2$VAI there is a pseudogap, in Mn$_2$VAI the X site (Mn) $t_{2g}$ DOS is displaced to higher energies, and forms a partially occupied band with width $\approx 1.5$ eV. This same Mn $t_{2g}$ character in the majority shifts downward (from the exchange splitting) and is the cause of opening the majority spin band gap that leads to HM magnetism.

In Fe$_2$VAI the conduction band states just above $E_F$ are purely V $e_g$ in character. In Mn$_2$VAI the DOS within nearly 0.5 eV of the Fermi level, both above and below, are dominated by Mn $t_{2g}$ character. The main onset of V $e_g$ character has been pushed nearly 1 eV upward by the exchange splitting and the resulting changes in bonding.
IV. SUMMARY

We have shown that the GGA exchange-correlation functional leads to an increase of 40% (0.1 eV) in the bandgap in the majority bands leading to a HM band structure for Mn$_2$VAl, whereas LDA predicted band overlap in the majority channel. Since there is no reason to expect the structure in the high symmetry Heusler lattice to distort (and no distortion has been observed), and we have used the most advanced exchange-correlation functional known at present, this result represents a robust prediction of modern electronic structure theory. Since colossal magnetoresistance has been associated with the HM state in the ferromagnetic manganites and also apparently in the double perovskite Sr$_2$FeMoO$_6$, this compound gives another clear example to explore the relation between half-metallicity and large magnetoresistance.

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