Majority-spin non-quasiparticle states in half-metallic ferrimagnet $\text{Mn}_2\text{VAI}$

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The density of non-quasiparticle states in the ferrimagnetic full-Heuslers $\text{Mn}_2\text{VAI}$ alloy is calculated from first principles upon appropriate inclusion of correlations. In contrast to most half-metallic compounds, this material displays an energy gap in the majority-spin spectrum. For this situation, non-quasiparticle states are located below the Fermi level, and should be detectable by spin-polarized photoemission. This opens a new way to study many-body effects in spintronic-related materials.

Half metals display a particular type of itinerant-electron magnetism as well as unusual electronic properties: they are metallic for one spin channel, and insulating or semiconducting for the opposite one [1, 2]. Electronic structure calculations based on density functional theory offer an explanation for the half-metallicity based on the interplay between the crystal structure, the valence electron count, the covalent bonding, and the large exchange splitting in addition to symmetry constraints. The expected 100% spin polarization of half-metals turned out to be an excellent motivation in developing the field of spintronics both from a theoretical and an experimental point of view [2, 3]. In reality many potential half-metallic ferromagnets exhibit a dramatic decrease of bulk spin polarization at temperatures well below their Curie temperature. In order to understand such a behavior from a theoretical point of view it is necessary to consider finite temperature many-body effects [2].

An important effect of dynamical electron correlations in half-metals is the existence of non-quasiparticle (NQP) states [4, 5, 6]. These states contribute significantly in reducing the tunneling transport in heterostructures containing HMF [6, 7, 8, 9, 10, 11], even in the presence of disorder. NQP states strongly influence the value of disorder. NQP states are located below the Fermi level, and should be detectable by spin-polarized photoemission. This opens a new way to study many-body effects in spintronic-related materials.

Contrary, for negative $I$ the minority-spin band lies below the majority-spin one [2, 6]. Occupied minority-spin states can be superposed with majority-electron states plus magnons, with conserved total spin projection and thus zero-point magnon fluctuations are allowed. It is the fluctuations which are responsible for formation of occupied majority-electron NQP states there.

Formally, the difference between $I < 0$ and the previous $I > 0$ cases, can be explained in terms of a particle-hole transformation $c_{i\sigma} \rightarrow d_{i\bar{\sigma}}$, and $d_{i\sigma} \rightarrow c_{i\bar{\sigma}}$. This modifies the $s-d$ exchange Hamiltonian into $I \sum \textbf{S}_i \sigma_{i\alpha} d_{i\alpha} d_{i\beta}$.
In other words, the Hamiltonian with $I > 0$ for electrons is equivalent to that with $I < 0$ for holes.

The above argument based on the $s$-$d$ exchange model can be generalized for arbitrary multi-band half-metallic electronic structures. The conclusion remain unchanged: for the case of minority-electron gap, NQP states are situated above the Fermi energy, while for the cases when the gap is present for majority-electrons, NQP states are formed below the Fermi energy.

Most HMF materials have a gap in the minority spin channel so that NQP states arise above the Fermi level. As a consequence, these states cannot be studied by the very well-developed and accurate technique of spin-polarized photoemission, which can only probe occupied states. The spin-polarized Bremsstrahlung Isochromat Spectroscopy (BIS) probing unoccupied states has a much lower resolution. For this reason, HMF with a gap in the majority-spin channel, and, consequently, NQP states in the occupied region of the spectrum, allow for a detailed experimental analysis of these correlation-induced states and are, therefore, potentially of great interest. It is the purpose of the present work to perform an electronic structure calculation based on a combination of the generalized-gradient approximation (GGA) and of DMFT for the half-metallic ferrimagnetic full-Heusler alloy Mn$_2$VAI, which has a gap in the majority spin channel. By appropriately taking into account effects due to electronic correlations, we demonstrate explicitly the existence of majority spin NQP states arising just below the Fermi level, and study the temperature dependence of their spectral weight.

In full Heusler compounds with the formula X$_2$YZ, Mn atoms usually occupy the Y-position, while compounds in which Mn assumes the X-position Mn$_2$YZ, are very rare. The prototype from the latter category is Mn$_2$VAI, for which a large number of theoretical and experimental investigations have been made. Neutron diffraction experiments demonstrated the existence of a ferrimagnetic state in which Mn has a magnetic moment of $1.5 \pm 0.3 \mu_B$ and V moment is $-0.9 \mu_B$. X-ray diffraction and magnetization measurements found a total magnetic moment of $1.94 \mu_B$ at 5K, close to the half-metallic value of $2 \mu_B$. The Curie temperature of the sample was found to be about 760K and the loss of half-metallic character was attributed to the small amount of disorder. Electronic-structure calculations performed by Ishida within the local-density approximation (LDA), predict the ground state of Mn$_2$VAI to be close to half-metallicity. Weht and Pickert used the GGA for the exchange correlation potential and showed that Mn$_2$VAI is a half-metallic ferrimagnet with atomic moments in very good agreement with the experiment. Recent calculations of the exchange parameters for Mn$_2$VAI show a strong $Mn-V$ exchange interaction that influence the ordering in the Mn sublattice. The estimated Curie temperatures are in good agreement with the experimental values. The intermixing between V and Al atoms in the Mn$_2$VAI alloy showed that a small degree of disorder decreases the spin polarization at the Fermi level from its ideal 100% value, but the resulting alloy Mn$_2$VAI$_{1-x}$Al$_{1+x}$ still show an almost half-metallic behavior.

According to the ideal full Heusler ($L_2_1$) structure, the V atom occupy the $(0, 0, 0)$ position, the Mn atoms are situated at $(1/4, 1/4, 1/4)a$ and $(3/4, 3/4, 3/4)a$, and the Al at $(1/2, 1/2, 1/2)a$, where $a = 5.875\AA$ is the lattice constant of the Mn$_2$VAI compound. In our work, correlation effects in the valence V and Mn $d$ orbitals are included via an on-site electron-electron interaction in the form $\frac{1}{2} \sum_{\mathbf{m}_1,\sigma} U_{\mathbf{m}_1m'_1\sigma} c_{\mathbf{m}_1\sigma}^\dagger c_{\mathbf{m}_1\sigma} c_{\mathbf{m}'_1\sigma} c_{\mathbf{m}'_1\sigma}$. The interaction is treated in the framework of dynamical mean field theory (DMFT) with a spin-polarized T-matrix Fluctuation Exchange (SPTF) type of impurity solver. Here, $c_{\mathbf{m}\sigma}^\dagger c_{\mathbf{m}\sigma}$ destroys/creates an electron with spin $\sigma$ on orbital $m$ on lattice site $\mathbf{i}$. The Coulomb matrix elements $U_{\mathbf{m}_1m'_1\sigma}$ are expressed in the usual way in terms of three Kanamori parameters $U, U' = U - 2J$ and $J$. Typical values for Coulomb ($U = 2eV$) and Stoner ($J = 0.93eV$) parameters were used for Mn and V atoms. The above value of $U$ is considerably smaller than the bandwidth of Mn$_2$VAI (7–8eV) therefore the use of a perturbative SPTF-solver is justified. In addition, the same solver was used to investigate spectroscopic properties of transition metals with remarkable results.

Since the static contribution from correlations is already included in the local spin-density approximation (LSDA/GGA), so-called “double counted” terms must be subtracted. To achieve this, we replace $\Sigma(E)$ with $\Sigma(E) - \Sigma(0)\sigma$ in all equations of the DMFT procedure. Physically, this is related to the fact that DMFT only adds dynamical correlations to the LSDA/GGA result. For this reason, it is believed that this kind of double-counting subtraction “$\Sigma(0)$” is more appropriate for a DMFT treatment of metals than the alternative static “Hartree-Fock” (HF) subtraction.

In Fig. we present the total density of states computed in GGA and GGA+DMFT, for $T=200K$. The GGA density of states displays a gap of about 0.4eV in the majority spin channel in agreement with previous calculations. As expected from the $s$-$d$ model calculation, majority spin NQP states are visible just below the Fermi level, with a peak around $-0.25eV$. In order to evaluate the spectral weight of these NQP states, we fit the low-energy density of states below the Fermi level in the majority channel with a Gaussian centered around the peak position. The NQP spectral weight is then defined as the area below the Gaussian curve. The inset shows the NQP spectral weight for several temperatures up to 300K. It is interesting to note that within the computed temperature range $50 \leq T \leq 300$ these values are almost constant and considerably larger in comparison with similar values for (NiFe)MnSb. The data pre-
FIG. 1: (color online) Total density of states, computed within GGA (dashed/blue) and GGA+DMFT (full/red). The Gaussian fit to the density of NQP states is shown as a dotted-dashed (black) line just below the Fermi level for the majority spin channel. The temperature dependent spectral weight of NQP states is displayed in the inset. The Gaussian fit to the density of NQP states is shown as a dotted-dashed (black) line just below the Fermi level for the majority spin channel. The temperature dependent spectral weight of NQP states is displayed in the inset.

The atom resolved DOS is presented in Fig. 2. In GGA, the net magnetic moment per unit cell is $2\mu_B$ with parallel Mn moments having values close to $1.6\mu_B$ and oppositely oriented V moments close to $-0.8\mu_B$. Below the gap, the majority spin total DOS is mainly of Mn character. The Mn and V moments have a strong $t_{2g}$ character, and a small Al contribution to the magnetic moment is present. Most of the V majority spin states lie above the gap, along with the Mn $e_g$ states. Minority-spin states below 0.5eV have roughly an equal amounts of $V(t_{2g})$ and Mn character. States around the Fermi energy have a predominant $Mn(t_{2g})$ character, in agreement with [24]. In contrast to the GGA results, the many-body DMFT calculation (see Fig. 2) yields a significant DOS for the majority spin states just below the Fermi level. These are the majority spin NQP states discussed above [12, 13, 15, 16, 17, 18]. As can be seen in Fig. 2, majority spin NQP states are predominantly of $Mn - 3d^5$ character. Their spectral weight is quite significant (see inset of Fig. 1) so that accurate spin-polarized photoemission experiments should be able to identify the existence of such states. In contrast, majority spin $V(t_{2g})$ states below the Fermi energy are not significantly changed. Above the Fermi level, the $Mn(e_g)$ and $V(e_g)$ states are pushed to higher energy, such that a gap is formed just above $E_F$. In the minority spin channel below $E_F$, both V and Mn($t_{2g}$) states are slightly modified, while above $E_F$, V($e_g$) states are shifted to higher energies by 0.5eV. Around the Fermi level, the dominant $Mn - 3d^5$ DOS is not significantly changed with respect to the GGA values.

The applicability of the local DMFT approach to the problem of the existence of NQP states has been discussed in ref. [2] and [14]. It is essential to stress that the accurate description of the magnon spectrum is not important for the existence of nonquasiparticle states and for the proper estimation of their spectral weight, but can be important to describe an explicit shape of the density of states “tail” in a very close vicinity of the Fermi energy.

The imaginary part of the atom and orbital resolved self-energies, for T=200K are presented in Fig. 3. For the minority $Mn-e_g$, $V-e_g$ and $V-t_{2g}$ orbitals we observe that the imaginary part of the self-energy has a rather symmetric energy dependence around the Fermi level, with a normal Fermi-liquid-type behavior $-Im\Sigma_{Mn/V}^\dagger(E) \propto$
The behavior of the imaginary part of the self-energy \( \text{Im}\Sigma_{Mn/V}(E) \) shows a significant increase right below the Fermi level which is more pronounced for the \( t_{2g} \)-orbitals. In addition, a slight kink is evidenced for an energy around -0.25\,eV. These results shown in Fig. 3 suggests that many-body effects are stronger on Mn than on V sites. Therefore, NQP states are mainly determined by the Mn-d atoms.

The effect of disorder on half-metallicity was recently discussed in Mn\(_2\)V\(_{1-x}\)Al\(_{1+x}\) alloys, for \(-0.2 \leq x \leq 0.2\). The excess of both Al and V atoms \((x=0.1/-0.1 \text{ or } x=0.2/-0.2)\) has the effect of shrinking the gap to zero, but with the Fermi level situated within the gap. In addition, the Mn moment is not affected by disorder and remains constant, in contrast to the V moment. Spin polarization is decreased by about 10%, with electrons around the Fermi level having a dominant minority spin character. In contrast, many-body correlations have a much more dramatic effect. For non-zero temperatures, all atomic magnetizations are decreased. For instance, near room temperature \((T = 300\,K)\) the strongest decrease occurs in V, for which the moment drops almost by 47%, the Mn moment is reduced by 32%, while the AI experiences just a small reduction by 4%. As one can see from Fig. 4, already at 50\,K polarization drops to 75%, and is further decreased upon increasing the temperature. As we discussed previously for half-metals in the presence of NQP states [2, 11, 14, 15, 16, 17, 18], namely that magnetization and polarization behave differently as function of temperature. However, as can be seen in Fig. 4 this difference is not as sharp as in other HMF materials [12, 18].
the case of FeMnSb \[16\], many-body induced depolarization is significantly stronger than the effect of disorder or of other spin-mixing mechanisms such as spin-orbit coupling. This observation seems to hold also for the case of Mn$_2$VAI, although we can not exclude the fact that for a larger degree of disorder, the material could possibly depart from its almost half-metallic situation displayed for small degree of substitution ($-0.2 < x < 0.2$).

In conclusion, in this paper we have shown for a specific material that NQP states are also present in half-metals with a gap in the majority spin channel, and appear just below the Fermi level, as predicted in model calculations \[12\]. In the case of Mn$_2$VAI, these states mainly consist of Mn-3$d^9$ electrons and have a considerable spectral weight. Although this material was reported to be a half-metal from electronic structure calculations \[24\], the experimental evidence is not clear. Several reasons are invoked such as existence of defects or the reduced symmetry at surface and interfaces. From a theoretical point of view, we show that correlation-induced NQP states significantly change the majority spin electronic states, thus reducing the spin polarization at $E_F$. The appearance of NQP states and its connection with tunneling magnetoresistance was recently studied in Co$_2$MnSi-based tunnel magnetic junction \[12\]. A great challenge would be to produce TMR junctions based on the ferri-magnetic Mn$_2$VAI. This would allow for a direct experimental investigation of the existence of majority spin NQP states. Promising candidate HMF materials with a majority spin gap of similar magnitude as Mn$_2$VAI are the double perovskites Sr$_2$FeMoO$_6$ (M=Mo,Re) or Sr$_2$CrReO$_6$ often associated with collosal magnetoresistance behavior. In particular the electronic structure of Sr$_2$CrReO$_6$ shows a closure of its majority spin gap in the presence of spin-orbit coupling \[37\], with states having a small spectral weight symmetrically distributed around the Fermi energy. Discrepancies between the experiment and theoretical computations were explained based on possible antiposite disorder \[37\]. We suggest that a significant density of NQP states could be present in the above perovskites as well. Work on these lines is in progress.

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