Chapter 6

Magnetism of Half-Metallic Heusler Compounds

6.1 Introduction

This chapter is devoted to the study of half-metallic Heusler compounds because of their potential applications in the field of spintronics. The concept of half-metallicity and its origin is introduced in chapter 4. In these systems at the Fermi energy $E_F$ one spin direction is metallic and the other has an energy gap, resulting in 100% spin polarization while normal transition metal ferromagnets (Fe, Co, and Ni) possess the spin polarization of 40% - 50%. Consequently, half-metallic ferromagnets are expected to provide the huge tunnel magnetoresistance (TMR) and giant magnetoresistance (GMR) in magnetoelectronics devices. They can also be used as perfect spin filters and spin-injection devices as an alternative to ferromagnetic 3$d$ metals. Since 3$d$ systems cause serious problems due to large difference between the resistances of metal and semiconductor substrate.

Among the half-metallic ferromagnets the Heusler compounds are much more suitable for device applications due to their very high Curie temperatures, low coercivities and crystal structure compatibility with the zincblende semiconductors used industrially. Recently, several groups achieved very large TMR values using half-metallic Heusler alloys.

Our extensive investigations on ferromagnetic Heusler alloys (non-half metallic) presented in the preceding chapter provided a clear physical picture for the exchange coupling mechanism, in particular the role of conduction electrons in mediating interactions between Mn atoms is revealed. In principle, the same discussion also holds for the half-metallic Heusler compounds considered in this chapter. The only difference is that in these systems the calculated pattern of exchange interactions are rather short range. This behavior originates from the absence of Fermi surface for one spin direction in half-metallic ferromagnets which introduce an additional damping factor in RKKY model.

However, in this chapter we will discuss rather specific problems related to the nature of magnetism in half-metallic Heusler compounds aiming to provide a guideline for the further
6.2 NiMnSb, CoMnSb, Co$_2$CrAl and Co$_2$MnSi compounds

Experimental studies. For experimentally well established systems like NiMnSb and Co$_2$MnSi (section 6.2) we consider effect of the half-metallic gap on the stability of exchange interactions and resulting Curie temperature by contracting the lattice spacing which moves the position of Fermi level within the gap. Role of the inter-sublattice exchange interactions is revealed for the formation of very high Curie temperatures in some full Heusler compounds such as Co$_2$MnSi. We also study spin wave spectra and temperature dependence of the magnetization employing multi-sublattice Green function technique within Tyablikov decoupling scheme. In section 6.3 we demonstrate the role of the strong antiferromagnetic intersublattice exchange interactions in establishing ferrimagnetic order. Last section of this chapter is reserved for the discussion of predicted new semi Heusler compounds with very high $T_C$. Last part of this section dwells on an important problem which is the relation between half metallicity and Curie temperature by the example of these new systems.

6.2 NiMnSb, CoMnSb, Co$_2$CrAl and Co$_2$MnSi compounds

Recently, these compounds received considerable theoretical and experimental interest as promising device candidates due to their high Curie temperatures, large minority-spin band gaps and the possibility to grow on common semiconductors.

Experimental investigations were in the direction of the utilization of these materials in fundamental spintronics devices. Kämmerer et al. integrated Co$_2$MnSi, as a representative of the full-Heusler compound family, as one magnetic electrode in magnetic tunnel junctions and found a tunnelling magnetoresistance effect much larger than in the case that the Ni$_{0.8}$Fe$_{0.2}$ or Co$_{0.3}$Fe$_{0.7}$ are used as magnetic electrodes [90]. Similar experiments have been undertaken by Okamura and collaborators using Co$_2$Cr$_{1-x}$Fe$_x$Al as the magnetic electrode [91]. Girgis et al. have fabricated current-in-plane giant magnetoresistive (GMR) devices based on multilayers of epitaxial NiMnSb and sputtered Cu and CoFe. They measured magnetoresistance of up to 3.5% at room temperature [92].

On the theoretical side, the studies are mainly focused on the stability of the half-metallic gap under different circumstances. For NiMnSb and Co$_2$MnSi compounds it was shown that half-metallicity is preserved under tetragonalization of the crystal lattice [93]. For a number of Heusler alloys Mavropoulos et al. studied the influence of the spin-orbit coupling on the spin-polarization at the Fermi level and found the effect to be very small [94] that is in agreement with a small orbital moment calculated by Galanakis. [95] Larson et al. [96] have shown that the structure of Heusler alloys is stable with respect to the interchange of atoms and Orgassa and collaborators and Picozzi and collaborators have demonstrated that a small degree of disorder does not destroy the half-metallic gap. [97, 98] Dowben and Skomski have shown that at non-zero temperatures the spin-wave excitations lead to the presence at the Fermi level of the electron states with opposite spin projections leading to decreasing spin-polarization of the charge carriers [99].

Despite very strong interest to the half-metallic ferromagnetism in Heusler alloys the
6.2. NiMnSb, CoMnSb, Co$_2$CrAl and Co$_2$MnSi compounds

Figure 6.1: (a) Calculated spin-resolved density of states of NiMnSb and CoMnSb for three values of the lattice parameter. (b) The same for Co$_2$CrAl and Co$_2$MnSi. The upper panels present the results for the experimental lattice constant [50]. The middle panels show the results for the lattice parameter $a_{II}$ that is determined by the coincidence of the Fermi level with the upper edge of the half-metallic gap. The bottom panels present the results for lattice parameter $a_{III}$ that is obtained by a 1% contraction of $a_{II}$.

study of the exchange interactions and finite temperature magnetic properties received less attention. The latter constitutes the main purpose of the present section. Here we study the exchange interactions and Curie temperatures in both half- and full-Heusler alloys for three different lattice spacings. The investigation of the influence of the value of the lattice parameter on the properties of the Heusler alloys is important since the samples grown on different substrates can have different lattice spacings. The last part of this section is devoted to the consideration of the temperature dependence of magnetization at the experimental lattice parameters.

6.2.1 Effect of lattice parameter on magnetic properties

In this subsection we report the calculation of density of states, magnetic moments, interatomic exchange interactions and Curie temperatures at different lattice parameters for all four compounds.

- NiMnSb and CoMnSb

The electronic structure of both compounds has been extensively studied earlier and the reader is referred to the review [100] and references therein for detailed discussion. Here we present a brief description of the calculational results aiming to provide the basis for further considerations and to allow the comparison with previous work.
In Table 6.1 we collect the atomic and total spin moments for three different lattice parameters. The first calculation is performed for the experimental bulk lattice constant \( a_0 \). The calculated densities of states (DOS) for this case are presented in the upper panel of Fig. 6.1. For both NiMnSb and CoMnSb the Fermi level lies in the low-energy part of the half-metallic gap. The compression of the lattice pushes the majority \( p \) states to higher energies that results in increased energy position of the Fermi level with respect to the half-metallic gap. At the lattice parameter \( a_{II} \) the Fermi level coincides with the upper edge of the gap (Fig. 6.1). In the next step we further contracted the lattice constant by 1\% (lattice parameter \( a_{III} \), bottom panel in Fig. 6.1). In this case the Fermi level is slightly above the gap and the total spin moment is slightly smaller than the integer values of 3 and 4 \( \mu_B \) for CoMnSb and NiMnSb respectively.

The contraction of the lattice leads to an increase of the hybridization between the \( d \) orbitals of different transition-metal atoms. This results in a decrease of the spin moment of Mn. In the case of NiMnSb this change is small: the reduction of the Mn spin moment under lattice contraction from the experimental lattice parameter to \( a_{II} \) is \( \sim 0.2 \mu_B \). The Ni spin moment increases by about the same value to preserve the integer value of the total spin moment of 4 \( \mu_B \).

In CoMnSb, the half-metallic gap is larger than in NiMnSb. As a result, the transition of the Fermi level to the upper gap-edge requires a large lattice contraction of 11\% (Table 6.1). This leads to a strong decrease of the Mn moment by 0.84 \( \mu_B \). To compensate this decrease the Co moment changes its sign transforming the magnetic structure from ferrimagnetic to ferromagnetic.

In Fig. 6.2 we present the exchange constants calculated for various lattice spacings. The Co-Co, Ni-Ni exchange interactions as well as the exchange interactions between the moments of the 3\( d \) atoms and the induced moments of Sb atoms are very weak and are not shown. The weakness of the effective Co-Co and Ni-Ni exchange interactions can be explained by a relatively large distance between atoms and relatively small atomic moments.

On the other hand, each Ni(Co) atom is surrounded by four Mn atoms as nearest neighbors that results in strong Mn-Ni(Co) exchange interaction (Fig. 6.2). Also the exchange interaction between large Mn moments is strong.

The ferromagnetic Mn-Mn interactions are mainly responsible for the stable ferromagnetism of these materials. For both systems and for all lattice spacings studied the leading Mn-Mn exchange interaction is strongly positive. In NiMnSb, the Mn-Ni interaction of the nearest neighbors is positive for all three lattice parameters leading to the parallel orientation of the spins of the Mn and Ni atoms. In CoMnSb the situation is different. At the experimental lattice parameter the leading Mn-Co interaction is negative resulting in the ferrimagnetism of the system. For the contracted lattices the interaction changes sign resulting in the ferromagnetic ground state of the alloy.

The analysis of the strength of the exchange interaction as a function of the lattice parameter shows that in CoMnSb the contraction leads to a strong increase of both leading
6.2. NiMnSb, CoMnSb, Co$_2$CrAl and Co$_2$MnSi compounds

Table 6.1: Calculated atom-resolved and total spin moments in $\mu_B$ for NiMnSb, CoMnSb, Co$_2$CrAl and Co$_2$MnSi. All compounds are half-metallic at the experimental lattice constants taken from Ref. [50]. $a_{II}$ means the use of the lattice constant that places the Fermi level at the upper edge of the half-metallic gap and $a_{III}$ corresponds to 1% contraction of the lattice constant with respect to $a_{II}$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>a(Å)</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
<th>Void</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiMnSb - $a_{[exp]}$</td>
<td>5.93</td>
<td>0.20</td>
<td>3.85</td>
<td>-0.09</td>
<td>0.04</td>
<td>4.00</td>
</tr>
<tr>
<td>NiMnSb - $a_{II}$</td>
<td>5.68</td>
<td>0.32</td>
<td>3.68</td>
<td>-0.05</td>
<td>0.05</td>
<td>4.00</td>
</tr>
<tr>
<td>NiMnSb - $a_{III}$</td>
<td>5.62</td>
<td>0.33</td>
<td>3.64</td>
<td>-0.04</td>
<td>0.05</td>
<td>3.97</td>
</tr>
<tr>
<td>CoMnSb - $a_{[exp]}$</td>
<td>5.87</td>
<td>-0.32</td>
<td>3.41</td>
<td>-0.11</td>
<td>0.02</td>
<td>3.00</td>
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<td>CoMnSb - $a_{II}$</td>
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<td>0.45</td>
<td>2.57</td>
<td>-0.06</td>
<td>0.04</td>
<td>3.00</td>
</tr>
<tr>
<td>CoMnSb - $a_{III}$</td>
<td>5.17</td>
<td>0.48</td>
<td>2.52</td>
<td>-0.05</td>
<td>0.04</td>
<td>2.99</td>
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<tr>
<td>Co$<em>2$CrAl - $a</em>{[exp]}$</td>
<td>5.74</td>
<td>0.62</td>
<td>1.83</td>
<td>-0.08</td>
<td></td>
<td>3.00</td>
</tr>
<tr>
<td>Co$<em>2$CrAl - $a</em>{II}$</td>
<td>5.55</td>
<td>0.69</td>
<td>1.68</td>
<td>-0.06</td>
<td></td>
<td>3.00</td>
</tr>
<tr>
<td>Co$<em>2$CrAl - $a</em>{III}$</td>
<td>5.49</td>
<td>0.69</td>
<td>1.66</td>
<td>-0.05</td>
<td></td>
<td>2.99</td>
</tr>
<tr>
<td>Co$<em>2$MnSi - $a</em>{[exp]}$</td>
<td>5.65</td>
<td>0.93</td>
<td>3.21</td>
<td>-0.06</td>
<td></td>
<td>5.00</td>
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<tr>
<td>Co$<em>2$MnSi - $a</em>{II}$</td>
<td>5.49</td>
<td>0.97</td>
<td>3.10</td>
<td>-0.04</td>
<td></td>
<td>5.00</td>
</tr>
<tr>
<td>Co$<em>2$MnSi - $a</em>{III}$</td>
<td>5.43</td>
<td>0.97</td>
<td>3.01</td>
<td>-0.04</td>
<td></td>
<td>4.97</td>
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</table>

Mn-Co and Mn-Mn interactions. On the other hand, in NiMnSb the increase of the Mn-Ni interaction is accompanied by a decrease of the leading Mn-Mn interaction. Simultaneously, the interaction between the second-nearest Mn atoms increases with contraction in the case of NiMnSb staying almost unchanged in CoMnSb. This complexity of the behavior reflects the complexity of the electronic structure of the systems.

The interatomic exchange parameters are used to evaluate the Curie temperature within two different approaches: MFA and RPA. In Table 6.2 we present the values of the Curie temperature obtained, first, by taking into account the Mn-Mn interactions only and, second, with account for both Mn-Mn and Mn-Ni(Co) interactions. The contribution of the inter-sublattice interactions to the Curie temperature appears to be less than 5% for both compounds and the Curie temperature is mainly determined by the intra-sublattice Mn-Mn interaction.

The MFA and RPA estimations of the Curie temperature differ rather strongly (Table 6.2). The relative difference of two estimations is about 20%. The reason behind this difference will be discussed below. For the systems considered here the RPA estimations of the Curie temperatures are in good agreement with the experiment, somewhat overestimating the experimental values.

Recently Kübler [101] reported estimations of the Curie temperature of NiMnSb. His approach is based on the evaluation of the non-uniform magnetic susceptibility on the basis of the Landau-type expansion for the free energy. Within some approximations the parameters
used in the study of the thermodynamical properties can be expressed in terms of the quantities evaluated within the first-principles DFT calculations. The estimated values of the Curie temperature are 601 K for a static approach and 701 K if the frequency dependence of the susceptibility is taken into account. These estimations are somewhat lower than the value of 880 K given by the RPA approach (Table 6.2). A detailed comparative analysis of the two calculational schemes is needed to get an insight in the physical origin of this difference.

The contraction of the lattice in the case of the NiMnSb compound leads to an increase of the Mn-Ni interactions (Fig. 6.2). This results in increased difference between the Curie temperatures calculated with the Mn-Mn interactions only and with both Mn-Mn and Ni-Mn interactions taken into account (Table 6.2). For CoMnSb, the leading exchange interactions of both Mn-Mn and Mn-Co types increase in the value under transition from the experimental lattice constant to \(a_{\text{II}}\) (Fig. 6.2). As a result, the Curie temperature increases with contraction by about 50%.

- **Co\(_2\)CrAl and Co\(_2\)MnSi**

The second group of materials studied in the paper is formed by the full-Heusler compounds Co\(_2\)MnSi and Co\(_2\)CrAl. The electronic structure of these systems has been studied earlier [68]. Compared to half-Heusler systems, the presence of two Co atoms per formula unit results in an increased coordination number of Co atoms surrounding Mn atoms (eight instead of four in CoMnSb). This leads to an increased hybridization between the 3d orbitals of the Mn and Co atoms. The spin moment of Co in Co\(_2\)MnSi is about 1 \(\mu_B\) that is considerably larger than the Co moment in CoMnSb. In Co\(_2\)CrAl the Co moment is about 1/3rd smaller than in Co\(_2\)MnSi that reflects a smaller value of the Cr moment compared to the Mn moment (Table 6.1).
Table 6.2: Calculated Curie temperatures. The second and third columns contain the $T_C^{MFA(RPA)}$ obtained with the account for Mn-Mn (Cr-Cr) interactions only. In the next two columns all interactions are taken into account. The last column presents the experimental values of the Curie temperature from Ref. [50].

<table>
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<tr>
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<tbody>
<tr>
<td>NiMnSb - $a_I[exp]$</td>
<td>1096</td>
<td>880</td>
<td>1112</td>
<td>900</td>
<td>730</td>
</tr>
<tr>
<td>NiMnSb - $a_{II}$</td>
<td>1060</td>
<td>853</td>
<td>1107</td>
<td>908</td>
<td>-</td>
</tr>
<tr>
<td>NiMnSb - $a_{III}$</td>
<td>1008</td>
<td>802</td>
<td>1063</td>
<td>869</td>
<td>-</td>
</tr>
<tr>
<td>CoMnSb - $a_I[exp]$</td>
<td>785</td>
<td>619</td>
<td>815</td>
<td>671</td>
<td>490</td>
</tr>
<tr>
<td>CoMnSb - $a_{II}$</td>
<td>1185</td>
<td>940</td>
<td>1276</td>
<td>1052</td>
<td>-</td>
</tr>
<tr>
<td>CoMnSb - $a_{III}$</td>
<td>1140</td>
<td>893</td>
<td>1252</td>
<td>1032</td>
<td>-</td>
</tr>
<tr>
<td>Co$_2$CrAl - $a_I[exp]$</td>
<td>148</td>
<td>141</td>
<td>280</td>
<td>270</td>
<td>334</td>
</tr>
<tr>
<td>Co$<em>2$CrAl - $a</em>{II}$</td>
<td>168</td>
<td>159</td>
<td>384</td>
<td>365</td>
<td>-</td>
</tr>
<tr>
<td>Co$<em>2$CrAl - $a</em>{III}$</td>
<td>164</td>
<td>154</td>
<td>400</td>
<td>379</td>
<td>-</td>
</tr>
<tr>
<td>Co$_2$MnSi - $a_I[exp]$</td>
<td>232</td>
<td>196</td>
<td>857</td>
<td>740</td>
<td>985</td>
</tr>
<tr>
<td>Co$<em>2$MnSi - $a</em>{II}$</td>
<td>142</td>
<td>118</td>
<td>934</td>
<td>804</td>
<td>-</td>
</tr>
<tr>
<td>Co$<em>2$MnSi - $a</em>{III}$</td>
<td>110</td>
<td>75</td>
<td>957</td>
<td>817</td>
<td>-</td>
</tr>
</tbody>
</table>

As in the case of the half-Heusler compounds discussed above, the variation of the lattice parameter leads to the change in the position of the Fermi level. At the experimental lattice parameter the Fermi level of Co$_2$CrAl lies in the lower part of the half-metallic gap while for Co$_2$MnSi it is close to the middle of the gap (Fig. 6.1b). The contraction of the lattice needed to place the Fermi level at the upper edge of the gap is smaller than for CoMnSb. As a result, the change in the magnetic moments is also relatively weak (Table 6.1).

The presence of an extra Co atom in the full-Heusler alloys makes the interactions more complex than in the case of the half-Heusler alloys. In CoMnSb the important interactions arise between nearest Mn atoms (Mn-Mn interactions) and between nearest Mn and Co atoms (Mn-Co interaction). In the case of Co$_2$MnSi (Fig. 6.3) the interactions between Co atoms at the same sublattice (Co-Co) and between Co atoms at different sublattices (Co$^1$-Co$^2$) must be taken into account. The cobalt atoms at different sublattices have the same local environment rotated by 90° about the [001] axis. The leading interaction responsible for the stability of the ferromagnetism is the Mn-Co interaction between Mn atoms and eight nearest Co atoms (Fig. 6.3). This interaction changes weakly with the contraction of the lattice. Our exchange parameters agree well with the parameters of Kurtulus et al. (Fig. 6.3) who also found the Co-Mn exchange interaction to be leading [124].

The interaction between nearest Co atoms at different sublattices (filled green spheres in Fig. 6.3) favors the ferromagnetism also and is stronger than the ferromagnetic interaction between the nearest Mn atoms (empty spheres). Although the spin moment of Mn atoms
Figure 6.3: (a) The exchange constants for Co$_2$CrAl as a function of the interatomic distance. (b) The same for Co$_2$MnSi. The left panels correspond to the experimental lattice constant, the middle and right panels to $a_{\text{II}}$ and $a_{\text{III}}$ parameters respectively. The superscripts 1 and 2 denote Co atoms belonging to different sublattices. For comparison, the exchange parameters of Co$_2$MnSi obtained in Ref. [124] at the experimental lattice parameter ($a_{\text{I}[\text{exp}]}$) are shown. The following symbols are used in the presentation: + for the Mn-Mn and Mn-Co interactions and ⋆ for the Co-Co and Co$^1$-Co$^2$ interactions.

is larger than the moment of Co atoms (Table 6.1) the opposite relation between exchange parameters can be the consequence of the smaller distance between the Co atoms: $a/2$ between the Co atoms and $\sqrt{2}a/2$ between the Mn atoms. An interesting feature of the intra-sublattice Mn-Mn and Co-Co interactions is different signs of the exchange parameters for different distances between atoms. This leads to a RKKY-like oscillations of the parameters (Fig. 6.3).

In Co$_2$CrAl the leading Cr-Co interactions (empty triangles) are much smaller than corresponding Mn-Co interactions in Co$_2$MnSi. On the other hand, the leading inter-sublattice ferromagnetic Co-Co interactions are comparable in both systems. The compression of the lattice leads to an increase of the magnitude of the inter-sublattice Co-Cr and Co$^1$-Co$^2$ coupling. The intra-sublattice Cr-Cr and Co-Co interactions oscillate with varying inter-atomic distances.

The difference in the properties of the exchange parameters of the half- and full-Heusler alloys is reflected in the calculated Curie temperatures (Table 6.2). In contrast to CoMnSb where the Mn-Mn exchange interactions are dominant, in Co$_2$MnSi they play a secondary role. The $T_{\text{C}}^{\text{MFA}(\text{RPA})}$ calculated taking into account these interactions only is much smaller than the Curie temperature calculated with all inter-atomic exchange interactions taken into account (Table 6.2). The same conclusion is valid for Co$_2$CrAl where the Cr-Cr interactions give about half of the Curie temperature obtained with all interactions included into
A striking feature of the full Heusler compound $\text{Co}_2\text{CrAl}$ that differs it strongly from the half-Heusler systems considered in the previous Section is a very small difference between the $T_C$ values calculated within the MFA and RPA approaches. A similar behavior was obtained for the Curie temperatures of the zincblende MnSi and MnC [102]. In $\text{Co}_2\text{MnSi}$, the relative difference of the MFA and RPA estimations assumes an intermediate position between the half-Heusler systems and $\text{Co}_2\text{CrAl}$.

To understand the origin of the strong variation of the relative difference of the MFA and RPA estimations of the Curie temperature we compare in Fig. 6.4 the frozen magnon dispersions for two compounds. The magnons correspond to the Mn sublattice in the case of NiMnSb and to the Cr sublattice in the case of $\text{Co}_2\text{CrAl}$. As seen from Table 6.2 the MFA and RPA estimations obtained with the use of these dispersions differ by 20% for NiMnSb and by 5% for $\text{Co}_2\text{CrAl}$.

The Curie temperature is given by the average value of the magnon energies. In MFA this is the arithmetic average while in RPA this is harmonic average. Therefore we need to understand why for $\text{Co}_2\text{CrAl}$ these two averages are much closer than for NiMnSb. The following properties of the averages are important for us. The arithmetic average takes all the magnon values with equal weight whereas in the harmonic average the weight decreases with increasing energy of the magnon. It is an arithmetic property that the MFA estimation is larger than the RPA one or equal to it if all numbers to be averaged are equal to each other. In terms of magnon energies, $T_C^{\text{MFA}}$ is equal to $T_C^{\text{RPA}}$ in the case that the magnon spectrum is dispersion-less.

Considering the frozen-magnon dispersions from the viewpoint of these properties we indeed can expect that the arithmetic and harmonic averages will be closer for $\text{Co}_2\text{CrAl}$. In Fig. 6.4 both curves are scaled to have almost the same maximal value. It is seen that...
the \( \text{Co}_2\text{CrAl} \) dispersion has smaller relative contribution of the low-energy magnons because of the steeper increase of the curve at small wave vectors. It has also smaller contribution of the magnons with the largest energies because the maxima have the form of well-defined peaks opposite to \( \text{NiMnSb} \) where we get a plateau. Thus the main contribution in the case of \( \text{Co}_2\text{CrAl} \) comes from intermediate energies that makes the MFA and RPA estimations closer.

Coming back to the considerations of the Curie temperatures, we conclude that, in general, the Curie temperatures of \( \text{Co}_2\text{MnSi} \) and \( \text{Co}_2\text{CrAl} \) calculated within both MFA and RPA are in good agreement with experiment while the MFA values in the case of \( \text{NiMnSb} \) and \( \text{CoMnSb} \) overestimate the Curie temperature strongly.

The lattice contraction leads in both compounds to an enhancement of the Mn-Co(Cr-Co) exchange constants that results in an increase of the Curie temperature.

Kurtulus and collaborators have calculated the Curie temperature for \( \text{Co}_2\text{MnSi} \) within MFA and found the value of 1251 K that is considerably larger than our MFA estimate of 857 K. This difference is unexpected since the values of the exchange parameters obtained by Kurtulus et al. agree well with our parameters (Fig.6.3). To reveal the origin of the discrepancy we performed the MFA calculation of the Curie temperature with the exchange parameters of Kurtulus et al. and obtained the \( T_C \) value of 942 K which is in reasonable agreement with our estimate. Apparently the reason for the inconsistency is in the procedure of the solving of the multiple-sublattice MFA problem used by Kurtulus et al. that should deviate from the standard one [34].

### 6.2.2 Spin-wave spectra

In Fig. 6.5 we present the calculated spin-wave spectra for \( \text{NiMnSb} \) and \( \text{Co}_2\text{CrAl} \). The spin-wave energies are obtained by the diagonalization of the matrix of exchange parameters that contains all important intra- and inter-sublattice interactions. The number of branches in the spectrum is equal to the number of magnetic atoms in the unit cell: two in \( \text{NiMnSb} \) and three in \( \text{Co}_2\text{CrAl} \). One of the branches is acoustic and has zero energy for zero wave vector. Also in the spin-wave spectra, we see strong difference between two systems. In \( \text{NiMnSb} \), the acoustic branch is predominantly of the Ni type stemming from the weak interaction between Mn and Ni magnetic moments (see Fig. 6.2). On the other hand, the optical branch is of predominantly the Mn type. The strong hybridization between two sublattices is obtained only about \( q = 0 \). In \( \text{Co}_2\text{CrAl} \), the energy scale of the branches differs much smaller and the hybridization between sublattices is stronger than for \( \text{NiMnSb} \).

### 6.2.3 Temperature dependence of the magnetization

In this section we will present the results of the calculation of the temperature dependence of magnetization that is based on the consideration of the Heisenberg hamiltonian with exchange parameters calculated within a parameter-free DFT approach. To calculate the temperature dependence of the magnetization we use the RPA method as described in chapter 3. We
6.2. NiMnSb, CoMnSb, Co$_2$CrAl and Co$_2$MnSi compounds

Figure 6.5: The spin wave dispersions for NiMnSb and Co$_2$CrAl along the symmetry lines in the Brillouin zone. Filled and empty spheres denote the acoustic and optical branches, respectively.

consider both classical-spin and quantum-spin cases.

In the classical-spin calculations the calculated values of the magnetic moments (Table 6.1) are used. To perform quantum-mechanical RPA calculation we assign integer values to the atomic moments. In the semi Heusler compounds we ignore the induced moments on Ni and Co atoms and assign the whole moment per formula unit to the Mn atom: 4$\mu_B$ ($S = 2$) in NiMnSb and 3$\mu_B$ ($S = 3/2$) in CoMnSb. In Co$_2$MnSi we take the values of 3$\mu_B$ ($S = 3/2$) and 1$\mu_B$ ($S = 1/2$) for Mn and Co atoms respectively. This assignment preserves the value of the total spin moment per chemical unit. In Co$_2$CrAl we use in the quantum-RPA calculations the atomic moment of 2$\mu_B$ ($S = 1$) for Cr and 1$\mu_B$ ($S = 1/2$) for Co.

In Fig. 6.6(a), we present in the normalized form the calculated temperature dependence of the magnetization for both families of Heusler compounds. The calculations are performed for the experimental lattice parameter. For comparison, the experimental curves are presented. The nature of the spin (quantum or classical) influences the form of the curves considerably. The classical curve lies lower than the quantum one. This results from a faster drop of the magnetization in the low-temperature region in the case of classical spins. In general, the quantum consideration gives better agreement of the form of the temperature dependence of the magnetization with experiment.

In Fig. 6.6(b) we present the temperature dependence of the magnetization of individual sublattices. As expected from the previous discussions in half-Heusler systems the main contribution to the magnetization comes from the Mn sublattice while for the full-Heusler
6.2. NiMnSb, CoMnSb, Co₂CrAl and Co₂MnSi compounds

systems both 3d atoms contribute substantially.

Considering the calculated Curie temperatures we notice that the value of $T_C$ calculated within the quantum-mechanical RPA is substantially larger than the corresponding classical estimation (see Fig. 6.6). This property is well-known and has its mathematical origin in the factor $(S + 1)/S$ entering the RPA expression for the Curie temperature. In Fig. 6.7 we show the dependence of the Curie temperature calculated within the quantum mechanical RPA approach on the value of $S$. The exchange parameters are kept unchanged in these calculations. We see that the dependence has a monotonous character tending to a classical limit for large $S$.

Presently we do not have an explanation why quantum-mechanical calculations give better form of the temperature dependence while the classical calculation provides better value of the Curie temperature. We can suggest the following arguments. The quantum treatment is more appropriate than the classical one in the low-temperature region. At high temperatures characterized by strong deviation of the atomic spins from the magnetization axis the quantum treatment gives too slow decrease of the magnetization. It is worth noting that the consequent theory should take into account not only the orientational disorder of the atomic moments but also the single-particle (Stoner-type) excitations leading to the decrease of atomic moments. Another important aspect is related to the fact that the exchange parameters used in the calculations are estimated within the picture of classical atomic moments described above. It is possible that the values of the exchange parameters must be modified.
6.3 Competing Mn-Mn exchange interactions in ferrimagnetic 
Mn$_2$VZ ($Z = $ Al, Ge) compounds

Half-metallic ferrimagnetic materials, like FeMnSb or the Mn$_2$VAl compounds, are much more desirable than their ferromagnetic counterparts in magnetoelectronics applications. This is mostly due to the fact that the small value of the total magnetic moment in these systems provides additional advantageous. For example they do not give rise to strong stray fields in devices or are less affected by the external magnetic fields.

The ideal case for applications would be a half-metallic antiferromagnet like CrMnSb. It is a special antiferromagnet in the sense that the majority spin and minority spin densities of states are not identical, as for common antiferromagnets and the material is better described as a fully compensated ferrimagnet, having a magnetic moment that is, due to the half-metallic character, precisely equal to zero. Such a half-metallic antiferromagnet would be a very interesting magnetoelectronics material since it would be a perfectly stable spin-polarized electrode in a junction device. And moreover if used as a tip in a spin-polarized STM, it would not give rise to stray flux, and hence would not distort the domain structure of the soft-magnetic systems to be studied. Unfortunately, CrMnSb does not crystallize in the ordered C1$_b$ crystal structure adopted by the semi-Heusler alloys. However, these results show that such an important magnetoelectronics material could exist. Van Leuken and de Groot have recently suggested a possible route towards a half-metallic antiferromagnet starting from the semiconducting C1$_b$-type compound FeVSb [103]. It is isoelectronic with the non-existing half-metallic antiferromagnet CrMnSb. A 12.5% substitution of Mn for V,
6.3. Competing Mn-Mn exchange interactions in ferrimagnetic 
Mn$_2$VZ (Z = Al, Ge) compounds

Table 6.3: Lattice parameters, magnetic moments (in $\mu_B$) and mean-field estimation of the Curie temperatures for Mn$_2$VZ (Z= Al, Ge). The second (third) column gives the Curie temperature calculated with account for Mn-Mn (Mn-V) interactions only. In the fourth column both types of interactions are taken into account. The experimental value of Curie temperature for Mn$_2$VAl is taken from Ref.[50].

<table>
<thead>
<tr>
<th></th>
<th>a(Å)</th>
<th>Mn</th>
<th>V</th>
<th>Z</th>
<th>Cell</th>
<th>MF$_{[\text{Mn-Mn}]}$</th>
<th>MF$_{[\text{Mn-V}]}$</th>
<th>MF$_{[\text{all}]}$</th>
<th>Exp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn$_2$VAl</td>
<td>5.93</td>
<td>1.53</td>
<td>-0.03</td>
<td>0.93</td>
<td>2.00</td>
<td>30</td>
<td>623</td>
<td>638</td>
<td>760</td>
</tr>
<tr>
<td></td>
<td>5.87$^a$</td>
<td>1.50$^a$</td>
<td>-0.90$^a$</td>
<td>-0.10$^a$</td>
<td>2.00$^a$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.93$^b$</td>
<td>1.41$^b$</td>
<td>-0.79$^b$</td>
<td>-0.02$^b$</td>
<td>2.02$^b$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.92$^c$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn$_2$VGe</td>
<td>6.09</td>
<td>1.00</td>
<td>-0.04</td>
<td>1.00</td>
<td>-170</td>
<td>488</td>
<td>413</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.93$^b$</td>
<td>0.75$^b$</td>
<td>-0.48$^b$</td>
<td>-0.02$^b$</td>
<td>1.00$^b$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Ref.[106]
$^b$Ref.[68]
$^c$Ref.[104]

and (in order to keep the system isoelectronic, In for Sb) was predicted to already yield half-metallic ferrimagnetism, with local Mn moments of about 2.3 $\mu_B$ and a band gap of about 0.35 eV.

Here we consider experimentally well established Mn$_2$VAl compound and theoretically predicted Mn$_2$VGe compound. The latter one close to ideal case. Both systems have half-metallic ferrimagnetic ground state. Mn$_2$VGe is not yet synthesized. On the other hand, Mn$_2$VAl received much experimental and theoretical attention. The neutron diffraction experiment by Itoh et al. [40] gave the ferrimagnetic state of compound with Mn magnetic moment of 1.5$\pm$0.3$\mu_B$ and V moment $-0.9\mu_B$. Jiang et al. examined the magnetic structure of Mn$_2$VAl by X-ray diffraction and magnetization measurements [104]. They found that Mn$_2$VAl was nearly half-metallic with the total magnetic moment of 1.94$\mu_B$ at 5 K. The Curie temperature of the sample was found to be about 760 K and the loss of half-metallic character was attributed to the small amount of disorder. The electron structure calculation by Ishida et al. performed within the local-density approximation (LDA) to the density functional theory resulted in a ground state of Mn$_2$VAl close to half-metallicity [105]. Recently a detailed theoretical study of the magnetism of Mn$_2$VAl was reported by Weht and Pickett [106] who used the generalized gradient approximation (GGA) for the exchange correlation potential and have shown that Mn$_2$VAl is a half-metallic ferrimagnet with the atomic moments of 1.5$\mu_B$ and $-0.9\mu_B$ on Mn and V in very good agreement with experiment. The Fermi level was found to lie in the minority spin band.

Our main purpose here is a detailed study of the exchange interactions in two half-metallic Mn$_2$VZ compounds: Mn$_2$VAl and Mn$_2$VGe. It is shown that the pattern of exchange interactions in these systems deviates from the physical picture that can be expected on the basis
of the experimental information available [107]. Indeed, the Mn-Mn distance of 2.96Å(3.04Å) in \( \text{Mn}_2\text{VAl} \) (\( \text{Mn}_2\text{VGe} \)) is substantially smaller than the Mn-Mn distance of about 4.2Å in the \( \text{X}_2\text{MnZ} \)-type Heusler alloys [50]. (For \( \text{Mn}_2\text{VGe} \) we use the interatomic distance of \( \text{Mn}_2\text{VGa} \) [108]). On the other hand, it is comparable with the Mn-Mn distance in the antiferromagnetic fcc Mn (2.73Å) [109]. According to the Bethe-Slater curve [110] there are physical reasons to expect that smaller distances between the 3\(d\) atoms stimulate the formation of the antiferromagnetic structure whereas larger distances make the ferromagnetic structure energetically preferable. Among the Heusler alloys, a smaller distance between pairs of the Mn atoms is obtained in the case of random occupation by Mn and Z atoms of the Y and Z sublattices (see, e.g., the system with the B2-type crystal structure in Ref. [50]). Indeed, the experiment gives for such systems the antiferromagnetic ordering [50]. Therefore in the case of \( \text{Mn}_2\text{VAl} \) an antiferromagnetism of the two Mn sublattices can be expected. Our study shows, however, that the situation is more complex. Although a large magnetic moment is carried by Mn atoms, competing ferromagnetic (inter sublattice) and antiferromagnetic (intra sublattice) Mn-Mn interactions in \( \text{Mn}_2\text{VAl} \) almost cancel each other in the mean-field experienced by the Mn atoms. In \( \text{Mn}_2\text{VGe} \) the leading Mn-Mn exchange interaction is antiferromagnetic. In both compounds the ferromagnetism of the Mn subsystem is favored by strong antiferromagnetic Mn-V interactions.

The crystal structure is presented in chapter 4. The two Mn sublattices are equivalent. The nearest Mn atoms belong to two different sublattices. In Table 6.3 we present calculated magnetic moments. For comparison, the available experimental values of the moments and the results of previous calculations are given. The net magnetic moment per unit cell is \( 2\mu_B \) for \( \text{Mn}_2\text{VAl} \) and \( 1\mu_B \) for \( \text{Mn}_2\text{VGe} \). The magnetic alignment is ferrimagnetic in both systems. The Mn moments are parallel and assume the values close to \( 1.5\mu_B \) in \( \text{Mn}_2\text{VAl} \) and to \( 1\mu_B \) in \( \text{Mn}_2\text{VGe} \). The moment of V is close to \( -1\mu_B \) in both systems. The values of the moments are in agreement with the results of previous calculations.

- **Exchange parameters and Curie temperature**

The calculated Heisenberg exchange parameters are presented in figure 6.8. We obtained a strong dependence of the pattern of the Mn-Mn and V-V exchange interactions on the type of the Z atom. Actually, this is an expected result on the basis of our theoretical findings for the exchange mechanism in Heusler alloys presented in previous chapter. The nearest Mn-Mn distance is half of the lattice constant \( a \). The exchange interaction between the nearest Mn atoms is ferromagnetic (Fig. 6.8) for both compounds while second nearest neighbor interaction is antiferromagnetic. In both systems substantial Mn-Mn interactions reach only fourth nearest neighbor and show RKKY-type oscillations.

If only Mn-Mn exchange interactions are considered, in \( \text{Mn}_2\text{VAl} \) prevail ferromagnetic interactions while in \( \text{Mn}_2\text{VGe} \) the Mn-Mn dominate antiferromagnetic interactions. The corresponding Curie and Néel temperature are given in table 6.3.

The interactions between V atoms are very small and can be neglected. The formation of
the ferrimagnetic structure with all Mn moments being parallel to each other and the V moments directed oppositely is determined by the strong antiferromagnetic exchange interactions between the nearest Mn and V moments. In Mn$_2$VAl this interaction is 5 times larger than the nearest neighbor Mn-Mn interaction. In Mn$_2$VGe this factor increases to 10. The strong Mn-V antiferromagnetic coupling makes a parallel direction of the Mn moments surrounding a V atom energetically preferable leading to the ferromagnetism of the Mn sublattices. In Mn$_2$VGe this trend overcomes the direct antiferromagnetic Mn-Mn interaction.

In the 8th column of Table 6.3 we present the Curie temperature calculated with the Mn-Mn exchange interaction being neglected. The Curie temperature given in the last column takes into account both Mn-V and Mn-Mn interactions. It is clearly seen that the main contribution for both systems comes from the Mn-V interaction. In Mn$_2$VAl, the correction of $T_C$ due to the Mn-Mn exchange interaction is positive and very small. In Mn$_2$VGe, it is negative and amounts to 15%.

In Mn$_2$VAl, where the experimental estimation of the Curie temperature is available, both the theoretical and experimental values are in good agreement. The theoretical Curie temperature of Mn$_2$VGe should be considered as prediction.

6.4 Prediction of high $T_c$ in NiVAs and NiCrZ (Z = P, Se, Te) compounds

In recent years, the first-principles calculations have become established as a complementary tool to experiments in the design of new materials. In this section we illustrate this in the
Table 6.4: Lattice parameters, magnetic moments (in $\mu_B$) and MFA and RPA estimations of the Curie temperatures for NiVAs, NiCrZ (Z=P, Se, Te) and NiMnSb. The last column represents the relative difference of the MFA and RPA estimations.

<table>
<thead>
<tr>
<th></th>
<th>$a$(Å)</th>
<th>Ni</th>
<th>V,Cr,Mn</th>
<th>Void</th>
<th>Z</th>
<th>Cell</th>
<th>MFA</th>
<th>RPA</th>
<th>$\frac{MFA-\text{RPA}}{\text{RPA}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiVAs</td>
<td>5.85</td>
<td>-0.02</td>
<td>2.05</td>
<td>0.06</td>
<td>-0.09</td>
<td>2.0</td>
<td>723</td>
<td>603</td>
<td>% 20</td>
</tr>
<tr>
<td></td>
<td>5.87$^a$</td>
<td>-0.03</td>
<td>2.06</td>
<td>0.06</td>
<td>-0.09</td>
<td>2.0</td>
<td>715</td>
<td>595</td>
<td>% 20</td>
</tr>
<tr>
<td>NiCrP</td>
<td>5.59</td>
<td>-0.01</td>
<td>3.08</td>
<td>0.07</td>
<td>-0.15</td>
<td>3.0</td>
<td>1030</td>
<td>848</td>
<td>% 21</td>
</tr>
<tr>
<td></td>
<td>5.65$^b$</td>
<td>-0.06</td>
<td>3.16</td>
<td>0.06</td>
<td>-0.16</td>
<td>3.0</td>
<td>938</td>
<td>770</td>
<td>% 22</td>
</tr>
<tr>
<td>NiMnSb</td>
<td>5.93</td>
<td>0.19</td>
<td>3.86</td>
<td>0.04</td>
<td>-0.10</td>
<td>4.0</td>
<td>1096</td>
<td>880</td>
<td>% 24</td>
</tr>
<tr>
<td>NiCrSe</td>
<td>5.64</td>
<td>0.24</td>
<td>3.64</td>
<td>0.12</td>
<td>-0.01</td>
<td>4.0</td>
<td>537</td>
<td>508</td>
<td>% 6</td>
</tr>
<tr>
<td></td>
<td>5.65$^b$</td>
<td>0.23</td>
<td>3.65</td>
<td>0.12</td>
<td>-0.01</td>
<td>4.0</td>
<td>543</td>
<td>515</td>
<td>% 5</td>
</tr>
<tr>
<td>NiCrTe</td>
<td>5.84</td>
<td>0.24</td>
<td>3.68</td>
<td>0.11</td>
<td>-0.03</td>
<td>4.0</td>
<td>868</td>
<td>805</td>
<td>% 8</td>
</tr>
<tr>
<td></td>
<td>5.87$^a$</td>
<td>0.23</td>
<td>3.70</td>
<td>0.11</td>
<td>-0.03</td>
<td>4.0</td>
<td>874</td>
<td>812</td>
<td>% 8</td>
</tr>
</tbody>
</table>

$^a$ Lattice constant of InP  
$^b$ Lattice constant of GaAs

case of Ni-based half-metallic semi-Heusler compounds NiCrZ (Z=P, Se, Te) and NiVAs by calculating the magnetic phase transition temperatures. Our aim is to provide a guideline for experimental work, stimulating the fabrication of these new materials.

These systems were recently predicted to be half-metals [111, 112]. For each compound we performed calculations for two values of the lattice parameter (Table 6.4): the theoretical equilibrium parameter [111, 112] and the lattice parameter of a binary semiconductor that can be considered as a possible substrate for growing the corresponding Heusler alloy: GaAs for NiCrP and NiCrSe and InP for NiVAs and NiCrTe.

The two lattice parameters used in the calculations resulted for all systems in very similar physical properties (see, e.g., Table 6.4). Therefore the most of the results will be presented for one lattice constant. All the discussion in this section is valid for both lattice spacings.

- **DOS and magnetic moments**

In Fig. 6.9, we present the calculated electron densities of states (DOS) of the ferromagnetic phases of the four Heusler compounds. All systems are found to be half-metallic with the Fermi level lying in the semiconducting gap of the minority-spin channel. Our DOS are in good agreement with the DOS obtained in Refs.[111, 112].

In Table 6.4, the calculated magnetic moments are collected. Since the systems are half-metallic, the magnetic moments per formula unit are integer: $2\mu_B$ for NiVAs, $3\mu_B$ for NiCrP and $4\mu_B$ for NiCrSe and NiCrTe. The major part of the magnetic moment comes from the second formula atom (V,Cr). Small induced magnetic moments are found on Ni and sp atoms.
6.4. Prediction of high $T_c$ in NiVAs and NiCrZ (Z = P, Se, Te) compounds

Figure 6.9: Spin-projected density of states of NiVAs and NiCrZ (Z=P, Se, Te).

6.4.1 Frozen-magnon dispersions and exchange parameters

Figure 6.10(a) presents the frozen-magnon dispersion for NiCrZ (Z=P, Se, Te) and NiVAs. To compare we show the results for NiMnSb as well. The five systems can be subdivided into two groups. One group contains NiVAs, NiCrP and NiMnSb. Here the frozen-magnon dispersions are monotonous and resemble, visually, a simple cosinusoid. The second group contains NiCrSe and NiCrTe and is characterized by non-monotonous dispersions with a maximum close to the center of the q-interval (Fig. 6.10a). Note, that the sp elements (the third chemical-formula constituents) within each of the group belong to the same column of the Mendeleev’s table whereas for different groups these columns are different. The importance of the valency of the sp element for magnetic properties of Heusler alloys has been already observed in our earlier studies (see previous chapter).

The calculated exchange parameters are given in Fig. 6.10(b). Since the inter-atomic exchange parameters are the Fourier transforms of the frozen-magnon dispersions they reflect the properties of the dispersions: The exchange parameters belonging to the same group show similar qualitative behavior. On the other hand, there is strong difference between the systems belonging to different groups (Fig. 6.10(b)). In the first group (Fig. 6.10(b), left panel), the strongest exchange interaction takes place between nearest magnetic 3$d$ atoms. This strongest interaction determines the cosinusoidal form of the corresponding magnon dispersion. The sizable interaction between the second-nearest magnetic 3$d$ atoms describes the deviation of the dispersion from a simple cosinusoid.

In the second group of compounds (Fig. 6.10(b), right panel), the strongest interaction is between the second-nearest magnetic atoms. Because of the decreased period of the Fourier component corresponding to the second exchange parameter the dispersions are nonmonotonous and have the maximum not at the boundary of the Brillouin zone but inside
6.4. Prediction of high $T_c$ in NiVAs and NiCrZ (Z = P, Se, Te) compounds

A remarkable feature of the exchange interactions is their short range character: the leading contribution into the Curie temperature of all systems is provided by the interactions within the first two coordination spheres. The interactions with further coordination spheres are very weak and can be neglected in the calculation of the Curie temperature. The interactions between Ni atoms and the interactions of Ni with V and Cr are very weak and are not presented.

- **Curie temperature**

The calculated exchange parameters are used to evaluate the Curie temperature (Table 6.4). It is important to note that the similarity of the form of the magnon dispersions within one group of compounds is not accompanied by a quantitative closeness of the curves (Fig. 6.10a). Therefore the Curie temperatures can differ strongly for compounds belonging to the same group.

The Curie temperatures are estimated within two different schemes: MFA and RPA. For all systems and for both theoretical schemes the calculated Curie temperatures are substantially higher than room temperature. The MFA always gives the value of $T_c$ that is larger than the corresponding RPA value and usually overestimates the experimental Curie temperature.

The analysis of the calculational data allows to make a number of important conclusions. First, there is a strong influence of the $sp$ atom on the value of $T_c$. Indeed, the comparison of NiCrSe and NiCrTe that differ by the $sp$ atom shows that the Curie temperature changes

Figure 6.10: (a) Frozen-magnon dispersions for NiVAs, NiMnSb and NiCrZ (Z=P, Se, Te). The spectrum is shown for [0 0 q] direction in the reciprocal space. The wave vector is given in the units of $2\pi/a$. In the calculations only the V-V, Cr-Cr and Mn-Mn interactions were taken into account. (b) Interatomic exchange interactions. The calculational data for NiVAs and NiCrZ are presented for the theoretical equilibrium lattice constant.
6.4. Prediction of high $T_c$ in NiVAs and NiCrZ (Z = P, Se, Te) compounds from about 500 K in NiCrSe to about 800 K in NiCrTe. This strong dependence reveals the sensitivity of the exchange interactions and the Curie temperature to the details of the electron structure.

An interesting feature of the calculated Curie temperatures (Table 6.4) is a large difference between the MFA and RPA estimations for the first group of compounds in contrast to a small difference for the second group. Characterizing the relative difference of the MFA and RPA values of the Curie temperature by the relation $\frac{T_{c,\text{MFA}} - T_{c,\text{RPA}}}{T_{c,\text{RPA}}}$ we get for the first group of compounds a large value of 20-24% compared to a small value of 5-8% for the second group. This feature reflects the properties of the corresponding frozen-magnon spectra.

From Fig. 6.10(a) we see that the frozen-magnon curves of the second group of compounds are flat in the second half of the $q$ interval demonstrating here very weak dispersion. On the other hand, the first group of compounds have considerable dispersion in this part of the $q$ interval. In addition, the low-$q$ part of the curves for the second group of compounds lie higher than the corresponding part of the curves for the first group. Therefore, the relative contribution of the low-energy magnons to the RPA value of the Curie temperature is smaller in the second group of compounds. This combination of features of the wave-vector dependencies of the frozen-magnon energies is responsible for a larger difference between the RPA and MFA estimations of the Curie temperature of the first group of compounds.

6.4.2 Curie temperature and half-metallicity

An important question concerning the magnetism of the half-metallic systems is the relation between half-metallicity and Curie temperature. Indeed, a number of studies has shown that the half-metallicity can stimulate an increase of the Curie temperature [101, 113, 114]. The analysis of Fig. 6.11 allows us to establish a correlation between the value of the Curie temperature and the energy distance $\delta$ between the Fermi level and the upper edge of the semiconducting gap. This quantity determines the spacing between the highest occupied spin-up state and the lowest empty spin-down state. For very small $\delta$ of 0.03 eV in NiCrSe we obtained the lowest Curie temperature of 508 K. On the other hand, for large $\delta$ in NiCrP and NiMnSb we obtained the Curie temperature substantially above 800 K.

Since the value of the Curie temperature is determined by the magnetic excitations to interpret the $\delta - T_C$ correlation we need to understand the origin of the influence of the $\delta$ value on the spin-wave energies.

The magnon energies reflect the energy prize for the deviations of the atomic moments from parallel directions [6]. In the ground-state ferromagnetic configuration the spin-projection is a good quantum number and the electron states with opposite spin projections do not interact. The deviation of the atomic moments from parallel directions leads to the mixing of the majority-spin and minority-spin states. The hybridization of a pair of the states leads to their repulsion. As a result, the energy of the lower state decreases (bonding state) and the energy of the upper state increases (antibonding state). If the lower state is occupied and the
6.4. Prediction of high $T_c$ in NiVAs and NiCrZ ($Z = P, Se, Te$) compounds

Figure 6.11: Spin-projected density of states of NiVAs, NiCrP, NiMnSb, NiCrSe and NiCrTe near Fermi level. Also shown are the RPA estimations of the Curie temperature and the energy distances between the Fermi level and the bottom of the spin-down conduction band.

upper state is empty this process leads to the decrease of the energy of the magnon making ferromagnetic state energetically less favorable. The smaller is the energy distance between interacting states the stronger is the effect.

Coming back to the half-metallic compounds considered in the paper we note that the hybridizational interaction of this type takes place between the occupied majority-spin states below the Fermi level and the empty spin-down states at the bottom of the conduction band. The distance between these states is given by parameter $\delta$. Therefore this process provides a mechanism for the correlation between $\delta$ and Curie temperature.

Since the strength of the hybridizational repulsion increases with decreasing energy distance between interacting states the negative contribution to the spin-wave energies is larger in the case of smaller $\delta$. However, the correlation between parameter $\delta$ and $T_C$ or, more general, between the half-metallicity and $T_C$ should not be considered as a universal rule. The hybridizational repulsion considered above is only one of numerous processes arising in a complex multi-band system with the deviation of the atomic moments from the parallel directions. The combined result of these processes cannot be predicted without the direct calculation of the excitation energies. Such a calculation must take into account the complexity of the electron structure of a real system. Indeed, the comparison of NiVAs and NiCrTe shows that both systems have the same $\delta$ of 0.14eV. However, their Curie temperatures differ strongly.