Slater-Pauling Rule and Curie-Temperature of Co\(_2\)-based Heusler compounds.

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Abstract

A concept is presented serving to guide in the search for new materials with high spin polarization. It is shown that the magnetic moment of half-metallic ferromagnets can be calculated from the generalized Slater-Pauling rule. Further, it was found empirically that the Curie temperature of Co\(_2\) based Heusler compounds can be estimated from a seemingly linear dependence on the magnetic moment. As a successful application of these simple rules, it was found that Co\(_2\)FeSi is, actually, the half-metallic ferromagnet exhibiting the highest magnetic moment and the highest Curie temperature measured for a Heusler compound.

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I. INTRODUCTION

There is a growing interest in materials with high spin polarization. Half-metallic ferromagnets (HMF) seem to be the materials of choice for applications, due to their exceptional electronic structure. They are metals for one spin direction and semiconductors for the other. This means that the electrons are 100% spin polarized at the Fermi energy.

The present research concentrates on finding potential materials with high spin polarization in the class of Heusler compounds. Their half-metallicity with respect to the spin was predicted by de Groot [1] for half-Heusler and by Ishida [2] for Heusler compounds. The latter have the chemical formula $X_2YZ$ with $X$ and $Y$ being transition metals and $Z$ being a main group element. Heusler compounds crystallize in the $L2_1$ structure ($Fm\overline{3}m$). In particular, the $Co_2YZ$ compounds exhibit the highest Curie temperature and the highest magnetic moments per unit cell (see data in [3, 4]).

II. CALCULATION OF THE ELECTRONIC STRUCTURE

The electronic structure of most of the known ternary Heusler compounds was calculated in order to find their magnetic moments and magnetic type. The calculations were performed by means of the full potential linear augmented plane wave (FLAPW) method as provided by Wien2k [5]. The exchange correlation energy functional was parameterized within the generalized gradient approximation (GGA) [6]. The energy convergence criterion was set to $10^{-5}$. For $k$-space integration, a $20 \times 20 \times 20$ mesh was used resulting in 256 $k$ points of the irreducible part of the Brillouin zone.

Overall, the calculations were performed for 59 Heusler compounds based on $X_2$ and $Y$ being 3$d$ metals, 17 with only $X_2$ and 28 with only $Y$ being a 3$d$ metal, as well as some compounds containing rare earth metals. In the first two groups, the heavy 3$d$ elements (Mn, Fe, Co, Ni, and Cu) were placed on $X$ sites. In the first group, the $Y$ positions were occupied by Sc, ..., Ni with the restriction that the $Y$ element was always lighter than the element on $X$ positions or equal. For the third group, the $X$ position was occupied by the 4$d$ elements Ru, Rh, Pd, Ag or by the 5$d$ elements Ir, Pt, Au, and the $Y$ position mostly by light 3$d$ elements. It turned out that nearly all (if not paramagnetic) Co based compounds ($Co_2YZ$) should exhibit half-metallic ferromagnetism. The calculated magnetic moments
were used for an analysis by means of the Slater-Pauling rule as described in the following section.

A. Slater - Pauling rule for Heusler compounds

Slater [7] and Pauling [8] reported first that the magnetic moments \( m \) of 3d elements and their binary compounds can be described by the mean number of valence electrons \( n_V \) per atom. The rule distinguishes the dependence of \( m(n_V) \) into two regions. The first (closed packed structures: fcc, hcp) is the range of itinerant magnetism \( (n_V \geq 8) \) and the second (bcc) is the one of localized moments \( (n_V \leq 8) \), where Fe is a borderline case. According to Hund’s rule it is often favorable that the majority \( d \) states are fully occupied \( (n_{d\uparrow} = 5) \). Starting from \( m = 2n_\uparrow - n_V \), this leads to the definition of the magnetic valence to be \( n_M = 10 - n_V \) such that the magnetic moment per atom is given by \( m = n_M + 2n_{sp\uparrow} \).

Pauling gave a value of \( n_{sp\uparrow} \approx 0.3 \) for the second region. A plot of \( m \) versus magnetic valence \( (m(n_M)) \) is called the generalized Slater-Pauling rule, as described by Kübler [9]. In the case of localized moments, the Fermi energy is pinned in a deep valley of the minority electron density. This constrains \( n_{d\downarrow} \) to be approximately three with the result \( m \approx n_V - 6 - 2n_{sp\downarrow} \), for Fe and its bcc-like binary alloys (Fe-Cr, Fe-Mn, and partially Fe-Co). It was shown by Malozemoff et al. [10] using band-gap theory that these arguments hold principally also if using more realistic band structure models, even so they were initially derived from rigid band models. In particular, they have shown that the rule is still valid if metalloids are involved.

Half-metallic ferromagnets are supposed to exhibit a real gap in the minority density of states where the Fermi energy is pinned. The gap has the consequence that the number of occupied minority states has to be an integer. Thus, the Slater-Pauling rule will be strictly fulfilled with

\[
m_{HMF} = n_V - 6 \tag{1}
\]

for the spin magnetic moment per atom.

For ordered compounds with different kind of atoms it may be more convenient to use all atoms of the unit cell. In the case of 4 atoms per unit cell, as in Heusler (H) compounds, one has to subtract 24 (6 times the number of atoms) from the accumulated number of valence electrons \( N_V \) \( (s, d \) electrons for the transition metals and \( s, p \) electrons for the main group
element) to find the spin magnetic moment $M$ per unit cell:

$$M_H = N_V - 24. \tag{2}$$

This rule of thumb is strictly fulfilled for HMF only as first noted in \cite{9} for half-Heusler (hH) compounds ($M_{hH} = N_V - 18$). In both types of compounds ($X_2YZ$ and $XYZ$) the spin magnetic moment per unit cell becomes strictly integer for half-metallic ferromagnets. An already very small deviation from an integer value indicates that the HMF character is completely lost. This situation changes for alloys with non-integer site occupancies like the quaternaries $X_2Y_{1-x}Y'_xZ$. In such cases $M$ may become non-integer depending on the composition, even for the HMF state.

The Slater-Pauling rule relates the magnetic moment with the number of valence electrons, but is not formulated to predict a half-metallic ferromagnet. The gap in the minority states of Heusler compounds or other HMF has to be explained by details of the electronic structure (for examples see \cite{11, 12}).

III. RESULTS

Figure 1 shows the generalized Slater-Pauling behavior of selected Heusler compounds with 3$d$ transition metals on the X and Y sites in comparison to the magnetic elements Fe, Co, and Ni. The magnetic moments were calculated as described above. It is seen that the Co$_2YZ$ compounds strictly fulfill the Slater-Pauling rule, whereas other compounds exhibit pronounced deviations from the Slater-Pauling like behavior. The latter, however, do not exhibit half-metallic ferromagnetism.

Inspecting the other transition metal based compounds, one finds that compounds with magnetic moments above the expected Slater-Pauling value are X=Fe based. Those with lower values are either X=Cu or X=Ni based, with the Ni based compounds exhibiting higher moments compared to the Cu based compounds at the same number of valence electrons. Moreover, some of the Cu or Ni based compounds are not ferromagnetic independent of the number of valence electrons (not included in Fig.1). Besides Mn$_2$VAl and Ir$_2$MnAl, only compounds containing both, Fe and Mn, were found to exhibit HMF character with magnetic moments according to the Slater-Pauling rule.

Plotting the Curie temperatures ($T_C$) of the known, 3$d$ metal based Heusler compounds
FIG. 1: Slater-Pauling graph for Heusler compounds.
The Co$_2$ based Heusler compounds are marked by full dots. The elemental metals Fe, Co, and Ni are given for comparison.

FIG. 2: Curie-temperatures of X$_2$YZ Heusler compounds.
The line is found from a linear fit of the measured $T_C$ for Co$_2$-based compounds (full dots). The elemental metals Fe, Co, and Ni are given for comparison.

as function of their magnetic moment results seemingly in a linear dependence for Co$_2$YZ half-metallic Heusler compounds (see Fig.2). According to this plot, $T_C$ is highest for those half-metallic compounds that exhibit a large magnetic moment, or equivalent for those with a high valence electron concentration when comparing to the Slater-Pauling rule. By extrapolating a linear dependence, $T_C$ is estimated to be above 1000K in compounds with 6$\mu_B$, that is with 30 valence electrons per unit cell.

The origin of the seeming linear dependence is not clear at first sight. In the molecular field approach, the Curie temperature of a system with two magnetic sub-lattices (Co, Y)
will be given by:

\[
T_C = \frac{1}{2} \max \left( T_{Co} + T_Y \pm \sqrt{(T_{Co} - T_Y)^2 + 4T_{Co,Y}^2} \right) \tag{3}
\]

with the sub-lattice temperatures \[13\]

\[
\frac{3}{2}k_BT_i \propto J_iS_i(S_i+1). \tag{4}
\]

The \(T_i\) are proportional to the Heisenberg exchange integral \(J_i\) at site \(i = Co, Y\). \(S_i\) is the accompanied spin moment. \(T_{Co,Y} \propto J_{Co,Y}\) is a composite temperature. The \(J_i\) describe the interaction of the atom at site \(i\) with the hole crystal. \(J_{Co,Y}\) is the pair interaction parameter between Co and Y sites (for details see \[14\]).

The calculations revealed that the magnetic moments at Co and Y sites increase simultaneously with increasing \(n_V\). Thus the expected non-linearity with \(m\) has to be compensated by variation of the Heisenberg exchange to result in the nearly linear dependence on \(n_V\).

\(T_C \approx \max(T_{Co}, T_Y)\) is governed by the higher of the two sub-lattice Curie temperatures if \(T_{Co,Y}\) is small with respect to \(T_{Co}\) and \(T_Y\). For the Co\(_2\)YZ compounds this is \(T_Y\) as was also found for other Heusler compounds \[9\]. Using this restriction, the calculation yielded \(T_C = 1120\text{K}\) for \(\text{Co}_2\text{FeSi}\), in good agreement with the experiment.

As a practical test for the models given here, we revisited \(\text{Co}_2\text{FeSi}\). This compound was previously reported to have a magnetic moment of \(5.9\mu_B\) per unit cell at 10K and a Curie temperature of \(> 980\text{K}\) \[15\], whereas band structure calculations predicted only \(5.27\mu_B\) \[12\]. One expects, however, \(M = 6\mu_B\) for the spin moment and \(T_C\) to be clearly above 1000K, from the estimate given above. Polycrystalline \(\text{Co}_2\text{FeSi}\) samples were investigated \[16\] and X-ray diffraction confirmed the \(L2_1\) structure with a lattice parameter of \(a = 5.64\text{Å}\). Low temperature magnetometry gave a magnetic moment of \(5.97\mu_B\) per unit cell at 5K, in excellent agreement to the Slater-Pauling rule. The Curie temperature was found to be \((1100 \pm 20)\text{K}\). This value fits very well the nearly linear behavior shown in Fig\[2\]. All experimental findings are supported by recent band structure calculations revealing a half-metallic ferromagnet with a magnetic moment of \(6\mu_B\), if using appropriate parameters in the self consistent field calculations \[17\].
IV. CONCLUSION

In summary, it was shown how the Heusler compounds can be described in terms of the Slater-Pauling rule. This is particularly the case for Co$_2$YZ compounds that exhibit half-metallic ferromagnetism. Further, it was found that the Co$_2$YZ compounds exhibit a seemingly linear dependence of the Curie temperature on the magnetic moment. Using the practical example of Co$_2$FeSi, it turned out that the given rule of thumb works for both magnetic moment and $T_C$. The rules may be applied not only to ternary but also to quaternary compounds like Co$_2$Y$_{1-x}$Y'Z if stabilized in the $L2_1$ phase. Recent examples are Co$_2$Cr$_{1-x}$Fe$_x$Z (Z=Al,Ga) \[18, 19, 20\]. An experimental challenge will be to find Heusler compounds with magnetic moments above 6$\mu_B$ and to prove whether it is possible to find even higher $T_C$ in this class of materials. Co$_3$Z compounds crystallize in a hexagonal structure, unfortunately. Thus, one way to reach that goal may be to stabilize Co$_{2+x}$Fe$_{1-x}$Z in the $L2_1$ phase.

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