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Slater-Pauling rule and Curie temperature of Co$_2$-based Heusler compounds

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A concept is presented serving to guide in the search for 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. Furthermore, 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. © *2006 American Institute of Physics.* [DOI: 10.1063/1.2167629]

I. INTRODUCTION

There is a growing interest in materials with high spin polarization. Half-metallic ferromagnets (HMF) seem to be the material of choice for applications due to their exceptional electronic structure. They are metals for one spin direction and semiconductors for another. 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 *et al.*[1] for half-Heusler compounds and by Ishida *et al.*[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 Refs. 3 and 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 parametrized 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 3d metals, for 17 based only on being a X_2 3d metal, and for 28 based only on Y being a 3d metal, as well as some compounds containing rare-earth metals. In the first two groups, the heavy 3d 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 should always be lighter than or equal to the element on X positions. For the third group, the X position was occupied by the 4d elements Ru, Rh, Pd, and Ag or by the 5d elements Ir, Pt, and Au; the Y position was occupied mostly by light 3d 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.

Slater-Pauling rule for Heusler compounds

Slater[7] and Pauling[8] reported 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 (close-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 as $n_M = 10 - n_V$ 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 3 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 more realistic band-structure models are used; 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.
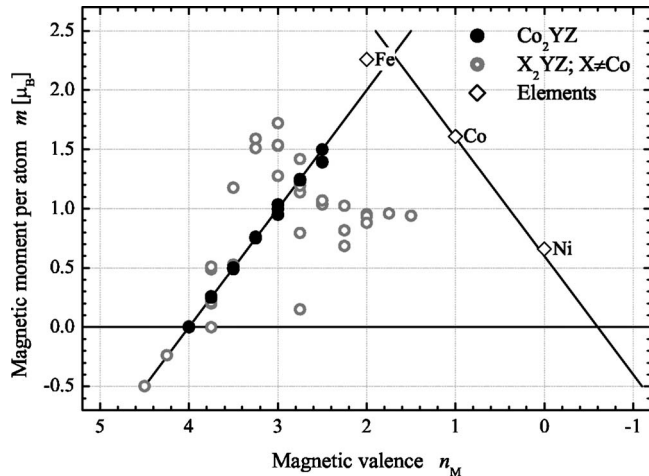
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FIG. 1. Slater-Pauling graph for Heusler compounds. The Co$_2$-based Heusler compounds are marked by full dots. The elemental metals Fe, Co, and Ni are given for comparison.

FIG. 2. Curie temperatures of X_2YZ 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.

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

$$m_{HMF} = n_V - 6 \qquad (1)$$

for the spin magnetic moment per atom.

For ordered compounds with different kinds of atoms it may be more convenient to use all atoms of the unit cell. In the case of four atoms per unit cell, as in Heusler (H) compounds, one has to subtract 24 (six 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:

$$M_H = N_V - 24. \qquad (2)$$

This *rule of thumb* is strictly fulfilled for HMF only, as noted in Ref. 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 noninteger site occupancies such as the quaternaries $X_2Y_{1-x}Y'_xZ$. In such cases M may become noninteger 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 Refs. 11 and 12).

III. RESULTS

Figure 1 shows the generalized Slater-Pauling behavior of selected Heusler compounds with 3d transition metals on the $X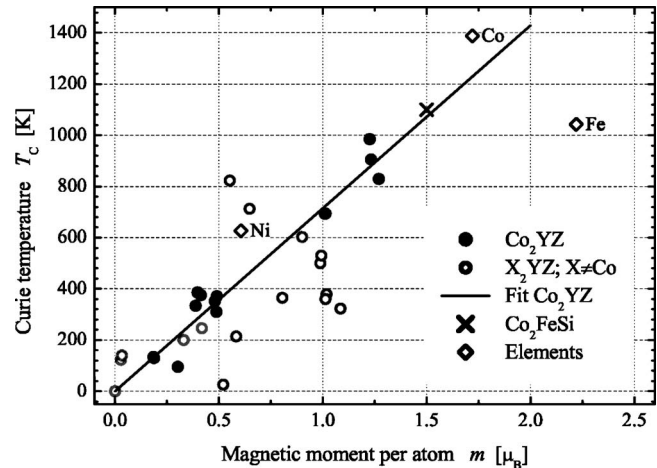$ and Y sites in comparison to the magnetic elements Fe, Co, and Ni. The magnetic moments were calculated as described above. It is seen that the Co$_2YZ$ compounds strictly fulfill the Slater-Pauling rule, whereas other compounds exhibit pronounced deviations from the Slater-Pauling-type behavior. The 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 based 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 a HMF character with magnetic moments according to the Slater-Pauling rule.

Plotting the Curie temperatures (T_C) of the known 3d-metal-based Heusler compounds as a function of their magnetic moment results seemingly in a linear dependence for Co$_2YZ$ 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 compared to the Slater-Pauling rule. By extrapolating a linear dependence, T_C is estimated to be above 1000 K 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 sublattices (Co, Y) will be given by

$$T_C = \tfrac{1}{2} \max(T_{Co} + T_Y \pm \sqrt{(T_{Co} - T_Y)^2 + 4T_{Co,Y}^2}) \qquad (3)$$

with the sublattice temperatures[13]

$$\tfrac{3}{2}k_B T_i \propto J_i S_i(S_i + 1). \qquad (4)$$

The T_i are proportional to the Heisenberg exchange integral J_i at site i=Co, Y. S_i is the accompanied spin moment.

$T_{\mathrm{Co},Y} \propto J_{\mathrm{Co},Y}$ is a composite temperature. J_i describes the interaction of the atom at site i with the hole crystal. $J_{\mathrm{Co},Y}$ is the pair-interaction parameter between Co and Y sites (for details see Ref. 14).

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

$T_C \approx \max(T_{\mathrm{Co}}, T_Y)$ is governed by the higher of the two sublattice Curie temperatures if $T_{\mathrm{Co},Y}$ is small with respect to T_{Co} and T_Y. For the Co_2YZ compounds this is T_Y, as was also found for other Heusler compounds.[9] Using this restriction, the calculation yielded $T_C = 1120$ K for Co_2FeSi, in good agreement with the experiment.

As a practical test for the models given here, we revisited Co_2FeSi. This compound was previously reported to have a magnetic moment of $5.9\mu_B$ per unit cell at 10 K and a Curie temperature of >980 K,[15] whereas band-structure calculations predicted only $5.27\mu_B$.[12] One expects, however, that $M = 6\mu_B$ for the spin moment and T_C to be clearly above 1000 K, from the estimate given above. Polycrystalline Co_2FeSi samples were investigated[16] and x-ray diffraction confirmed the $L2_1$ structure with a lattice parameter of $a = 5.64$ Å. Low-temperature magnetometry gave a magnetic moment of $5.97\mu_B$ per unit cell at 5 K, in excellent agreement with the Slater-Pauling rule. The Curie temperature was found to be (1100 ± 20) 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 appropriate parameters in the self-consistent-field calculations are used.[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_2YZ compounds that exhibit half-metallic ferromagnetism. Furthermore, it was found that the Co_2YZ compounds exhibit a seemingly linear dependence of the Curie temperature on the magnetic moment. Using the practical example of Co_2FeSi, 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 such as $Co_2Y_{1-x}Y'_xZ$ if stabilized in the $L2_1$ phase. Recent examples are $Co_2Cr_{1-x}Fe_xZ$ ($Z = Al, Ga$).[18–20] 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_3Z 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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