Doping of Mn_2VAl and Mn_2VSi Heusler alloys as a route to half-metallic antiferromagnetism

I. Galanakis,[1,*] K. Özdoğan,[2,†] E. Şaşıoğlu,[3,4,‡] and B. Aktaş[2]
[1]*Department of Materials Science, School of Natural Sciences, University of Patras, GR-26504 Patra, Greece*
[2]*Department of Physics, Gebze Institute of Technology, Gebze, 41400, Kocaeli, Turkey*
[3]*Institut für Festkörperforschung, Forschungszentrum Jülich, D-52425 Jülich, Germany*
[4]*Fatih University, Physics Department, 34500, Büyükçekmece, İstanbul, Turkey*
(Received 1 February 2007; published 28 March 2007)

Half-metallic antiferromagnets are the ideal materials for spintronic applications since their zero magnetization leads to lower stray fields and thus tiny energy losses. Starting from the Mn_2VAl and Mn_2VSi alloys we substitute Co and Fe for Mn and we show by means of first-principles electronic structure calculations that the resulting compounds are ferrimagnets. When the total number of valence electrons reaches the magic number of 24 the Fe-doped compounds are semimetals and thus nonmagnetic while the Co-doped ones show the desirable half-metallic antiferromagnetic character. The compounds are very likely to be synthesized experimentally since the parent compounds Mn_2VAl and Co_2VAl have been already grown in the Heusler $L2_1$ lattice structure.

DOI: 10.1103/PhysRevB.75.092407 PACS number(s): 75.47.Np, 75.30.Et, 75.50.Cc

Half-metallic ferromagnets (HMF's) are at the center of scientific research during the last decade due to their potential applications in spintronic devices.[1] These materials are ferromagnets where one of the two spin channels presents a gap at the Fermi level.[2] Several materials have been predicted theoretically based on first-principles calculations to present this peculiar behavior: several Heusler alloys,[3] some magnetic oxides and colossal magnetoresistance materials,[4] diluted magnetic semiconductors,[5] transition-metal pnictides and chalcogenides,[6] and Heusler semiconductors doped with high-valent transition metal atoms.[7] Heusler alloys are particularly attractive for applications due to their very high Curie temperatures and their structural similarity to widely used binary semiconductors like GaAs, InP, etc.

Although the research on HMF is intense, the ideal case would be a half-metallic antiferromagnet (HMA), also known as a fully compensated ferrimagnet, like the hypothetical Heusler MnCrSb (Ref. 8) or Mn_3Ga (Ref. 9) compounds, since such a compound would not give rise to stray flux and thus would lead to smaller energy consumption in devices. Unfortunately these alloys do not crystallize in the desired structure. In the absence of HMA's a lot of studies have been focused on the half-metallic ferrimagnets (HMFi's) which yield lower total spin moments than HMF's. van Leuken and de Groot have shown that doping of the semiconductor FeVSb results in such a material.[8] Also some other perfect Heusler compounds like FeMnSb (Ref. 10) and Mn_2VAl (Refs. 11–13) are predicted to be HMFi's. Recently other routes to half-metallic ferrimagnetism have been studied like the doping of diluted magnetic semiconductors[14] and the inclusion of defects in Cr pnictides.[15]

In this report we will study another route leading to the desirable HMA, the doping with Co of the Mn_2VAl and Mn_2VSi which are well known to be HMFi's. The importance of this route stems from the existence of Mn_2VAl in the Heusler $L2_1$ phase as shown by several groups.[16] Each Mn atom has a spin moment of around $-1.5\mu_B$ and each V atom a moment of about $0.9\mu_B$.[16] All theoretical studies on Mn_2VAl agree on the half-metallic character with a gap at the spin-up band instead of the spin-down band as for the other half-metallic Heusler alloys.[11–13,17] Şaşıoğlu and collaborators studied in detail the exchange interactions in the Mn_2VZ (Z=Al,Ge) HMFi's and showed that the antiferromagnetic coupling between the V and Mn atoms stabilizes the ferromagnetic alignment of the Mn spin moments.[13] Except Mn_2VAl, also the case of compounds with Ga, In, Si, Ge, and Sn instead of Al have been predicted to be HMFi's.[11]

In the following we will use the full-potential nonorthogonal local-orbital minimum-basis band structure scheme[18] (FPLO) in conjunction with the local density approximation to study the properties of the $[Mn_{1-x}X_x]_2VAl$ and $[Mn_{1-x}X_x]_2VSi$ compounds where X is Co or Fe. The coherent potential approximation is employed to ensure random doping of the lattice sites. We will show that doping with either Fe or Co keeps the HMFi of the ideal alloys respecting the Slater-Pauling (SP) rule (the total spin moment in the unit cell is the number of valence electrons minus 24).[12,22] When the concentration x is such that there are exactly 24 valence electrons the Co-doped compounds show the desirable HMA character contrary to the Fe-doped ones which lose their magnetic character and are simple semimetals. The Co-doped compounds are very likely to be synthesized experimentally since the parent compounds Mn_2VAl and Co_2VAl (Ref. 19) already exist.

We will start our discussion from the Co doping. Prior to the presentation of our results we have to note that due to the SP rule,[12] these compounds with fewer than 24 valence electrons have negative total spin moments and the gap is located at the spin-up band. Moreover, the spin-up electrons correspond to the minority-spin electrons and the spin-down electrons to the majority electrons contrary to the other Heusler alloys.[12] We have substituted Co for Mn in Mn_2V (Al or Si) in a random way, and in the upper panel of Fig. 1 we present the total density of states (DOS) as a function of the concentration x in $[Mn_{1-x}Co_x]_2VAl$ (solid black line) and $[Mn_{1-x}Co_x]_2VSi$ (red dashed line) for x=0.05, 0.1, and 0.2 (left column) and the atom-resolved DOS for x=0.1 in the top right panel. The perfect compounds show a region of low spin-up DOS (we will call it a "pseudogap") instead of a real

 ©2007 The American Physical Society

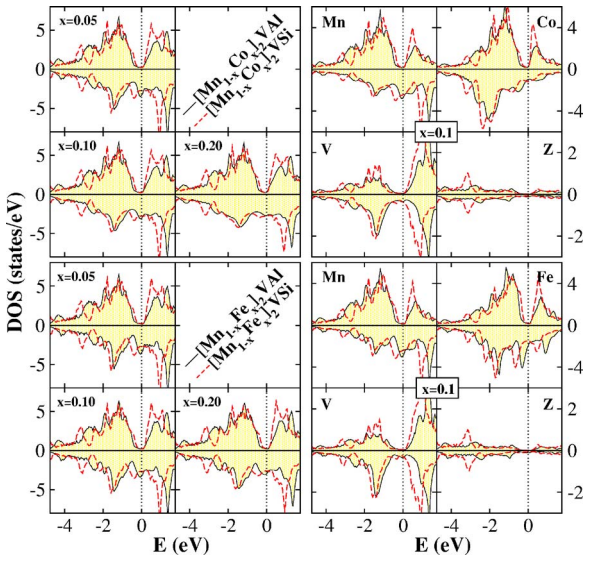

FIG. 1. (Color online) Top panel: total DOS as a function of the concentration x (left column) and atom-resolved DOS for $x=0.1$ (right panel) for the $[Mn_{1-x}Co_x]_2VAl$ and $[Mn_{1-x}Co_x]_2VSi$ compounds. Note that the atomic DOS have been scaled to one atom and Z corresponds either to Al or Si. The Fermi level has been chosen as the zero of the energy axis, and positive values of the DOS correspond to the spin-up (minority) electrons while negative values correspond to the spin-down (majority) electrons. Bottom panel: similar to the top panel for the $[Mn_{1-x}Fe_x]_2VAl$ and $[Mn_{1-x}Fe_x]_2VSi$ compounds.

gap. Upon doping the pseudogap at the spin-up band persists and the quaternary alloys keep the half-metallic character of the perfect Mn_2VAl and Mn_2VSi compounds. Co atoms are strongly polarized by the Mn atoms since they occupy the same sublattice and they form Co-Mn hybrids which afterwards interact with the V and Al or Si states.[12] The spin-up Co states form a common band with the Mn ones, and the spin-up DOS for both atoms has a similar shape. Mn atoms have less weight in the spin-down band since they accommodate less charge than the heavier Co atoms.

In Table I we have gathered the total and atom-resolved spin moments for all the Co-doped compounds as a function of the concentration. We have gone up to a concentration which corresponds to 24 valence electrons in the unit cell, thus up to $x=0.5$ for the $[Mn_{1-x}Co_x]_2VAl$ and $x=0.25$ for the $[Mn_{1-x}Co_x]_2VSi$ alloys. In the last column we have included the total spin moment predicted by the SP rule for the perfect half-metals.[12] A comparison between the calculated and ideal total spin moments reveals that all the compounds under study are half-metals with very small deviations due to the existence of a pseudogap instead of a real gap. Exactly for 24 valence electrons the total spin moment vanishes as we will discuss in the next paragraph. Co atoms have a spin moment parallel to the V one and antiparallel to the Mn moment, and thus the compounds retain their ferrimagnetic character. As we increase the concentration of Co atoms in the alloys, each Co has more Co atoms as neighbors, it hybridizes more strongly with them, and its spin moment increases while the spin moment of the Mn atom decreases (these changes are not too drastic). The *sp* atoms have a spin moment antiparallel to the Mn atoms as already discussed in Ref. 11.

TABLE I. Atom-resolved spin magnetic moments for the $[Mn_{1-x}Co_x]_2VAl$ and $[Mn_{1-x}Co_x]_2VSi$ compounds (moments have been scaled to one atom). The two last columns are the total spin moment (Total) in the unit cell calculated as $2[(1-x)m^{Mn}+xm^{Co}]+m^{V}+m^{Al\ or\ Si}$ and the ideal total spin moment predicted by the SP rule for half-metals (see Ref. 12). The lattice constants have been chosen as 0.605 nm for Mn_2VAl and 0.6175 for Mn_2VSi for which both systems are half-metals (see Ref. 11) and have been kept constant upon Co doping.

$[Mn_{1-x}Co_x]_2VAl$						
x	Mn	Co	V	Al	Total	Ideal
0	−1.573		1.082	0.064	−2.000	−2.0
0.025	−1.587	0.406	1.102	0.074	−1.899	−1.9
0.05	−1.580	0.403	1.090	0.073	−1.799	−1.8
0.1	−1.564	0.398	1.067	0.069	−1.600	−1.6
0.2	−1.522	0.412	1.012	0.059	−1.200	−1.2
0.3	−1.484	0.456	0.953	0.047	−0.804	−0.8
0.4	−1.445	0.520	0.880	0.034	−0.404	−0.4
0.5	−1.388	0.586	0.782	0.019	∼0	0
$[Mn_{1-x}Co_x]_2VSi$						
x	Mn	Co	V	Si	Total	Ideal
0	−0.960		0.856	0.063	−1.000	−1.0
0.025	−0.958	0.716	0.870	0.062	−0.900	−0.9
0.05	−0.944	0.749	0.860	0.059	−0.800	−0.8
0.1	−0.925	0.819	0.847	0.054	−0.600	−0.6
0.2	−0.905	0.907	0.839	0.046	−0.201	−0.2
0.25	−0.899	0.935	0.839	0.041	∼0	0

The most interesting point in this substitution procedure is revealed when we increase the Co concentration to a value corresponding to 24 valence electrons in the unit cell, thus the $[Mn_{0.5}Co_{0.5}]_2VAl$ and $[Mn_{0.75}Co_{0.25}]_2VSi$ alloys. The SP rule predicts for these compounds a zero total spin moment in the unit cell, and the electron population is equally divided between the two spin bands. Our first-principles calculations reveal that this is actually the case. The interest arises from the fact that although the total moment is zero, these two compounds are made up from strongly magnetic components. Mn atoms have a mean spin moment of $\sim -1.4\mu_B$ in $[Mn_{0.5}Co_{0.5}]_2VAl$ and $\sim -0.9\mu_B$ in $[Mn_{0.75}Co_{0.25}]_2VSi$. Co and V have spin moments antiferromagnetically coupled to the Mn ones which for $[Mn_{0.5}Co_{0.5}]_2VAl$ are $\sim 0.6\mu_B$ and $\sim 0.8\mu_B$, respectively, and for $[Mn_{0.75}Co_{0.25}]_2VSi$, $\sim 0.9\mu_B$ and $\sim 0.8\mu_B$. Thus these two compounds are half-metallic fully compensated ferrimagnets or, as they are best known in the literature, half-metallic antiferromagnets. To confirm the HMA character of these two compounds in Fig. 2 we have drawn the total and atom-resolved DOS of both compounds (bottom panel) together with the DOS of the parent Mn_2VAl and Mn_2VSi compounds (upper panel). The substitution of 50% of the Mn atoms by Co ones in Mn_2VAl leads to a smoothening of both the total and atom-projected DOS due to the hybridization between the Mn and Co atoms. Overall

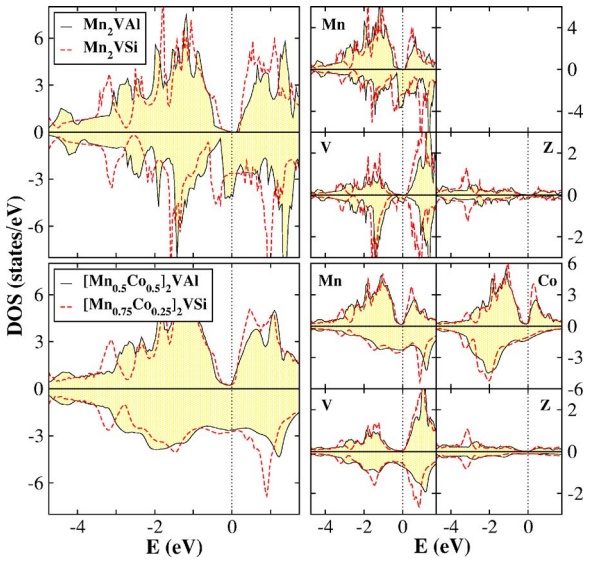

FIG. 2. (Color online) Top panel: total DOS (left column) and atom resolved DOS (right panel) for the perfect Mn_2VAl and Mn_2VSi compounds. Bottom panel: similar to the top panel for the Co-based half-metallic antiferromagnetic $[Mn_{0.5}Co_{0.5}]_2VAl$ and $[Mn_{0.75}Co_{0.25}]_2VSi$ compounds.

the energy position of the Mn states does not change and the Fermi level falls within the pseudogap in the spin-up band and in a region of high DOS in the spin-down band. All the remarks drawn in the previous paragraphs are still valid. A similar picture occurs also when substituting 25% of the Mn atoms by Co in Mn_2VSi. The case of $[Mn_{0.5}Co_{0.5}]_2VAl$ is of particular interest since both Mn_2VAl (Ref. 16) and Co_2VAl (Ref. 19) exist experimentally in the $L2_1$ structure of Heusler alloys and this quaternary compound seems very likely to be synthesized.

In the second part of our study we have investigated the effect of using Fe instead of Co. In the bottom panel of Fig. 1 we include the DOS for several concentrations and in Table II the total and atomic spin moments. The conclusions already drawn for the case of Co doping are valid also for the case of Fe doping. In the case of doping of Mn_2VAl the Fe moment is parallel to the Mn one and very small ($\sim 0.2\mu_B$) while the case of $[Mn_{1-x}Fe_xVSi]$ is similar to the Co case with Fe moment antiparallel to the Mn one. As we increase the concentration in Fe and reach Fe_2VAl and $[Mn_{0.5}Fe_{0.5}]_2VSi$, which have 24 valence electrons, the total spin moment vanishes. But our calculations indicate that instead of a HMA we get a nonmagnetic compound. To make the origin of this different behavior clear we present in Fig. 3 the calculated DOS for these compounds together with nonmagnetic calculations for the Co compounds. In Fe compounds the Fermi level falls within a pseudogap and the alloys act as the usual semimetals (these results agree with previous calculations by Weht and Pickett[20] while experiments suggest that Fe_2VAl exhibits heavy-fermionic behavior, being at the edge of becoming magnetic,[21] but such a discussion exceeds the scope of the present paper). Contrary, in the case of the nonmagnetic Co compounds, the Fermi level falls within a region of high DOS, and due to the Stoner criterion, the alloys prefer energetically the magnetic configuration. In the right column of Fig. 3 we present also the atomic DOS. V atoms have the same behavior in both cases, and the high DOS for the Co compounds arises from the Co-Mn hybrids. In Ref. 12 it was shown that the gap arises between the occupied t_{1u} and the unoccupied e_u states which are exclusively localized in space at the higher-valent transi-

TABLE II. Same as Table I for the Fe doping of the Mn sites. Note that when the total number of valence electrons is 24 we get a nonmagnetic semimetal.

$[Mn_{1-x}Fe_x]_2VAl$						
x	Mn	Fe	V	Al	Total	Ideal
0	−1.573		1.082	0.064	−2.000	−2.0
0.1	−1.604	−0.179	1.054	0.071	−1.799	−1.8
0.2	−1.602	−0.222	0.987	0.066	−1.599	−1.6
0.4	−1.572	−0.242	0.827	0.054	−1.199	−1.2
0.6	−1.498	−0.210	0.616	0.039	−0.796	−0.8
0.8	−1.315	−0.136	0.337	0.020	−0.387	−0.4
1.0	Nonmagnetic semimetal					
$[Mn_{1-x}Fe_x]_2VSi$						
x	Mn	Fe	V	Al	Total	Ideal
0	−0.960		0.856	0.063	−1.000	−1.0
0.1	−0.979	0.487	0.808	0.055	−0.800	−0.8
0.2	−0.961	0.437	0.718	0.045	−0.600	−0.6
0.3	−0.899	0.367	0.605	0.034	−0.400	−0.4
0.4	−0.726	0.257	0.446	0.021	−0.200	−0.2
0.5	Nonmagnetic semimetal					

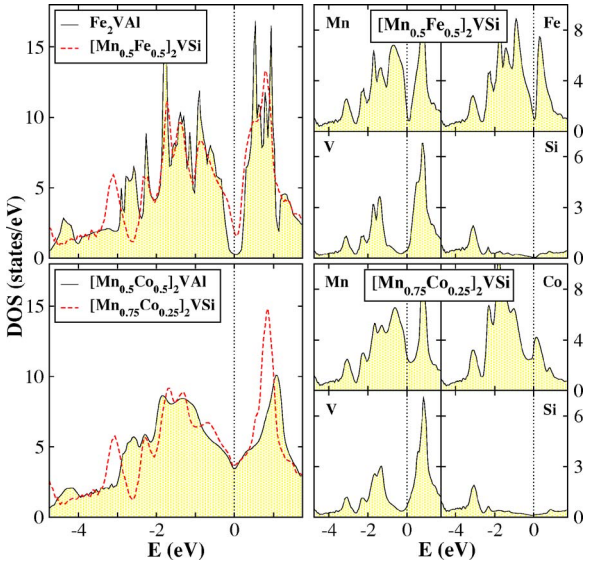

FIG. 3. (Color online) Left column: total DOS for the semimetals Fe_2VAl and $[Mn_{0.5}Fe_{0.5}]_2VSi$ (upper panel) and for nonmagnetic calculations of the $[Mn_{0.5}Co_{0.5}]_2VAl$ and $[Mn_{0.75}Co_{0.25}]_2VSi$ alloys (bottom panel). All four compounds have 24 valence electrons in the unit cell. Right column: atom-resolved DOS (scaled to one atom) for the $[Mn_{0.5}Fe_{0.5}]_2VSi$ and $[Mn_{0.75}Co_{0.25}]_2VSi$ compounds.

tion metal atoms, here the Fe-Mn or Co-Mn sites. In the case of Fe compounds, these states are well separated and the compound is a semimetal. In the case of the Co compounds, if they were nonmagnetic, these states strongly overlap due to the different positions of the Co-Mn hybrids, resulting in the high DOS at the Fermi level, and the alloys prefer the magnetic state (in Refs. 3 and 12 it was thoroughly investigated as to why this magnetic state prefers to be half-metallic).

We have studied the effect of doping the half-metallic ferrimagnets Mn_2VAl and Mn_2VSi. Both Fe and Co substitution for Mn keeps the half-metallic character of the parent compounds. When the total number of valence electrons reaches 24, the total spin moment vanishes as predicted by the Slater-Pauling rule. While in the case of Fe doping the 24-valence-electron compounds are nonmagnetic semimetals, in the case of Co doping half-metallic antiferromagnetism is achieved. The driving force is the different positions of the states exclusively composed by Mn-Co hybrids which strongly overlap, leading to very high values of the density of states at the Fermi level for the nonmagnetic phase and thus fulfilling the Stoner criterion for the appearance of magnetism. Thus we have presented an alternative way to create half-metallic antiferromagnets for realistic spintronic applications by simply introducing Co atoms in the Mn_2VAl and Mn_2VSi half-metallic ferrimagnets. Since crystals and films of both Mn_2VAl and Co_2VAl alloys have been grown experimentally, we expect these results to stimulate a strong interest in both theoretical and experimental research in the emerging field of spintronics.

*Electronic address: galanakis@upatras.gr
†Electronic address: kozdogan@gyte.edu
‡Electronic address: e.sasioglu@fz-juelich.de

[1] I. Žutić, J. Fabian, and S. Das Sarma, Rev. Mod. Phys. **76**, 323 (2004).
[2] R. A. de Groot, F. M. Mueller, P. G. van Engen, and K. H. J. Buschow, Phys. Rev. Lett. **50**, 2024 (1983).
[3] I. Galanakis, Ph. Mavropoulos, and P. H. Dederichs, J. Phys. D **39**, 765 (2006); I. Galanakis and Ph. Mavropoulos, cond-mat/0610827, J. Phys.: Condens. Matter (to be published).
[4] R. J. Soulen, Jr., *et al.*, Science **282**, 85 (1998); J.-H. Park, E. Vescovo, H.-J Kim, C. Kwon, R. Ramesh, and T. Venkatesan, Nature (London) **392**, 794 (1998).
[5] T. Jungwirth, J. Sinova, J. Mašek, J. Kučera, and A. H. MacDonald, Rev. Mod. Phys. **78**, 809 (2006).
[6] Ph. Mavropoulos and I. Galanakis, cond-mat/0611006, J. Phys.: Condens. Matter (to be published).
[7] B. R. K. Nanda and I. Dasgupta, J. Phys.: Condens. Matter **17**, 5037 (2005).
[8] H. van Leuken and R. A. de Groot, Phys. Rev. Lett. **74**, 1171 (1995).
[9] S. Wurmehl, H. C. Kandpal, G. H. Fecher, and C. Felser, J. Phys.: Condens. Matter **18**, 6171 (2006).
[10] R. A. de Groot, A. M. van der Kraan, and K. H. J. Buschow, J. Magn. Magn. Mater. **61**, 330 (1986).
[11] K. Özdoğan, I. Galanakis, E. Şaşıoğlu, and B. Aktaş, J. Phys.: Condens. Matter **18**, 2905 (2006).
[12] I. Galanakis, P. H. Dederichs, and N. Papanikolaou, Phys. Rev. B **66**, 174429 (2002).
[13] E. Şaşıoğlu, L. M. Sandratskii, and P. Bruno, J. Phys.: Condens. Matter **17**, 995 (2005).
[14] H. Akai and M. Ogura, Phys. Rev. Lett. **97**, 026401 (2006).
[15] I. Galanakis, K. Özdoğan, E. Şaşıoğlu, and B. Aktaş, Phys. Rev. B **74**, 140408(R) (2006).
[16] Y. Yoshida, M. Kawakami, and T. Nakamichi, J. Phys. Soc. Jpn. **50**, 2203 (1981); H. Itoh, T. Nakamichi, Y. Yamaguchi, and N. Kazama, Trans. Jpn. Inst. Met. **24**, 265 (1983); C. Jiang, M. Venkatesan, and J. M. D. Coey, Solid State Commun. **118**, 513 (2001).
[17] S. Ishida, S. Asano, and J. Ishida, J. Phys. Soc. Jpn. **53**, 2718 (1984); R. Weht and W. E. Pickett, Phys. Rev. B **60**, 13006 (1999).
[18] K. Koepernik and H. Eschrig, Phys. Rev. B **59**, 1743 (1999); K. Koepernik, B. Velicky, R. Hayn, and H. Eschrig, *ibid.* **58**, 6944 (1998).
[19] A. W. Carbonari, W. Pendl, Jr., R. N. Attili, and R. N. Saxena, Hyperfine Interact. **80**, 971 (1993).
[20] R. Weht and W. E. Pickett, Phys. Rev. B **58**, 6855 (1998).
[21] C. S. Lue, J. H. Ross, Jr., C. F. Chang, and H. D. Yang, Phys. Rev. B **60**, R13941 (1999).
[22] The number of valence electrons is calculated as $2[(1-x)z^{\mathrm{Mn}}+xz^{\mathrm{Co(Fe)}}]+z^{V}+z^{\mathrm{Al(Si)}}$ where z is the number of valence electrons of the corresponding chemical element.