Computational Study of Magnetic and Vibrational Properties of Fe₄Al₁₁₋ₓ and Fe₄Al₁₁₋ₓZnₓ

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We report first-principles calculations for Fe₄Al₁₁₋ₓ where 0 ≤ x ≤ 3 and for Fe₄Al₁₁₋ₓZnₓ for 0 ≤ y ≤ 1. We investigate the correlation of the magnetic and vibrational behavior with the density of states at the Fermi level. For Fe₄Al₁₁₋ₓ the magnitude of the magnetic moment correlates with the number of Fe in the chains. However we also find an intrinsic contribution to the magnetism associated with particular neighbor configurations, for Fe sites adjacent to the partially-occupied Al chains. The Fe content affects the density of states at the Fermi level by changing the magnitude of the spin majority, and as a result there are changing the magnetic properties. For Fe₄Al₁₁₋ₓZnₓ a reduction in the magnetization was observed with Zn substitution for Fe in the chains. There is a partial magnetic moment reduction for partial Zn substitution, but the magnetic moment is quenched when Zn fully substitutes for Fe in chain sites.

Index Terms—Magnetization, Magnetic Materials, Magnetic Properties, Aluminium Compounds.

I. INTRODUCTION

A number of complex structures are formed in the Al-rich Fe aluminides. These compounds also show a variety of different magnetic properties. In substitutional Fe in Al first principles and experimental results indicate that the substituted Fe impurity is nonmagnetic [1,2]. The mechanism for this behavior is attributed to spin fluctuations and not to the interaction of Fe with the host that quenches the moment as originally proposed. In contrast FeAl(2) is a strongly magnetic ordered intermetallic [3] with a local-moment residing on each Fe site [4]. Intermediate behavior is observed in Fe₂Al₆, where diluted moments are present and attributed plausibly to wrong site Fe occupation. Recently this material was also shown to exhibit anomalous vibrational properties [5] manifested in the specific heat at low temperatures. Here we address these properties through ab initio computational studies.

In fitting the crystallographic structure of Fe₂Al₅ [5] it was determined that the structure includes three different Al sites (Fig. 1). Al(1) sites (8/cell) are fully occupied, and along with Fe (4/cell) these sites make up a fixed framework for this structure. On the other hand the strongly overlapping sites Al(2) (4/cell) and Al(3) (8/cell) make up disordered chains. The Al(2) and Al(3) sites are partially occupied due to the closeness of these sites. These materials have an orthorhombic structure (Cmcm, s.g. #63). In addition, Zn may be substituted into this structure up to the composition Fe₄AlₓZn₁₋ₓ [6,7], apparently as simple substitution of Zn on chain sites for compositions up to Zn₁. These structures can be considered to be quasicrystalline approximants with pentagonal channels through which are threaded the one-dimensional arrays of partially occupied aluminium sites. Hopping of Al atoms between the channel sites may is presumably responsible for the anomalous vibrational behavior.

FIGURE 1 HERE

To understand the magnetic and vibrational behavior for these materials we therefore performed ab initio calculations on a number of superstructure configurations with different local bonding arrangements. These included superstructures of Fe₄Al₁₁₋ₓZnₓ with 0 < x < 1, and Fe₄Al₁₁₋ₓZnₓ with 0 < y < 1.

II. COMPUTATIONAL METHODS AND RESULTS

First-principles electronic structure calculations were implemented to understand the magnetic and structural properties. Spin polarized calculations were performed with the Full-Potential Linearized Augmented Plane-Wave method as implemented in the WIEN2k code [8] within the Perdew-Bruke-Ernzerhof formalism for the exchange-correlation term, and using the spin-dependent Generalized Gradient Approximation (GGA). All structures were minimized in volume and internal structural parameters.

In order to address the magnetization of wrong-site Fe atoms, we included several configurations with Fe on chain sites as well as with varying occupation of the partially filled Al(2) and Al(3) sites. This procedure also allowed us to address the possible presence of narrow features in the density of states near the Fermi level [9-11], as found in some quasicrystals and approximants. Therefore we examined the behavior of several distinct configurations of Fe₄Al₁₁₋ₓ with 0 ≤ x ≤ 3 and Fe₄Al₁₁₋ₓZnₓ with 0 < x < 1.

These superstructures were constructed starting with the parent Fe₂Al₅ configuration, for which the experimentally observed occupation of the chain sites is 0.36 for Al(2) and 0.23 Al(3), with Al(1) fully occupied [12]. For the first simulation we set the occupation to 0.25 for Al(2) and for Al(3) (thus placing one Al(2) and two Al(3) along the chain in each cell), making a net composition of Fe₂Al₁₁ (Fig. 1). To obtain this configuration Al was substituted in the chains spaced every fourth site counting along the chains, forming a 1×1×2 supercell in the original Cmcm (s.g. #63) symmetry. Once the substituted the symmetry of the system changes to monoclinic C2/m (s.g. #12). The Fe₄Al₁₁ configuration is a “filled-chain” configuration, with Al-Al spacings of 2.82 and 2.84 Å along the chain direction, compared with the Al-Al spacing in Al metal, 2.86 Å. However note that Fe₄Al₁₁ represents the upper limit of Al occupation, while the nominal composition as typically observed must include Al-Al...
spacings along the chains corresponding to non-bonding configurations.

Additional configurations considered included correspondingly larger Al-Al spacing along the chains. In the cases of Fe$_2$Al$_{10}$ and Fe$_2$Al$_8$ one and two Al atoms were removed from the filled-chain Fe$_2$Al$_{11}$ configuration, respectively. To investigate fractional occupation of Fe on chain sites, we also increased the Fe$_2$Al$_{11}$ superstructure size and substituted some of the Al(2) sites by Fe, for example Fe$_2$Al$_{9.33}$, representing a 1×1×2 supercell (Fe$_6$Al$_{12}$) with one chain site replaced by Fe, giving the composition Fe$_9$Al$_{12}$.

In the case of the Zn containing structures, to construct Fe$_2$Al$_{10}$Zn we took the parent structure Fe$_2$Al$_{11}$ and substituted one of the Al(2) sites by Zn. For Fe$_2$Al$_{10.5}$Zn$_{0.5}$ we made a 1×1×2 supercell based on Fe$_2$Al$_{11}$, and replaced one Al(2) atoms by Fe and one by Zn, giving the composition Fe$_9$Al$_{12}$Zn.

In Table I the eight different configurations considered are shown together with the supercell size in each case, and the number of Fe-occupied chain sites per formula unit. The last column indicates the computed magnetic moment of each configuration, per formula unit. The first five rows belong to Fe$_2$Al$_{11}$ configurations, and in these cases it is clearly seen that the magnetic moment increases as the number of Fe atoms along the chains increases, changing from 1.22 μ$_B$ for Fe$_2$Al$_{11}$, with zero Fe along the chains to 3.00 μ$_B$ for Fe$_2$Al$_{13}$, with 0.5 Fe along the chain per f.u. However we find that even without substitution of Fe on the chains, an intrinsic moment can appear in a way that is strongly dependent on the neighbor configuration. It seems that Fe along the chains is not the only thing that affects the magnetic moment. For example, Fe$_2$Al$_{11}$, only Al are placed along the chains and there is a large magnetic moment similar to the one with 0.25 Fe on the chain. This behavior might be the result of the Al being too close, remember that for this configuration there are 11 Al instead of the 10 from experimental results. Consequently it seems that the substitution of Al atoms very closely enhances the magnetic moment.

**TABLE I HERE**

For example, in the case of Fe$_2$Al$_{10}$ which is the same as the nominal composition Fe$_2$Al$_5$, the magnetic moment is small, similar behavior as previously measured in these compounds [5], confirming the above statement that too many Al in the chain give a high magnetic moment. In the case of Fe$_2$Al$_9$ a relatively high moment is found, as might be expected as the number of Fe-Al neighbors decreases [3]. However the filled-chain Fe$_2$Al$_{11}$ configuration also has a significant moment. The inclusion of Zn into the chains suppresses the magnetic moment; for example incorporation of 0.5 Zn per unit cell reduces the magnetic moment of Fe$_2$Al$_{10}$Zn$_{0.5}$ by 0.48 μ$_B$ compared with Fe$_2$Al$_{9.33}$. A more drastic change occurs when the Fe in the chains is fully substituted with Zn, in the Fe$_2$Al$_{11}$Zn configuration. In this case the magnetic moment completely disappears.

In Fig. 2 (a) and (b) the densities of states for spin up and spin down states, respectively, are shown. From the figures it can be observed that there exists a pseudogap at the Fermi level as expected for Hume-Rothery type materials. However there are also narrow features observed near the Fermi energy which can be correlated with the magnetic moments. In the case of Fe$_2$Al$_{11}$ the spin majority is for spin up, meanwhile for Fe$_2$Al$_8$ the spin down is the majority. On the other hand in Fe$_2$Al$_{10}$ spin up and spin down states are practically the same. The difference between the number spin up and spin down states in Fe$_2$Al$_{11}$ is 4.44 states/eV f.u., while for Fe$_2$Al$_8$ the difference is 2.34 states/eV f.u., but for Fe$_2$Al$_{10}$ the difference becomes zero.

FIGURE 2 HERE

**FIGURE 3 HERE**

In the case of Fe$_2$Al$_{11}$, Fig. 3 shows the d (non-spin-polarized) density of states. While most of the δ-states are below the Fermi level, a very narrow peak is observed at $E_F$. For this peak the density of states is strongly dominated by a Fe atom situated on a regular framework site having only one occupied chain Al site within 2.4 Å, whereas the other Fe sites have two such Al neighbors. The calculated moment is also strongly localized on this site. Thus it appears that the observed dilute magnetism includes an intrinsic feature associated with the different local neighbor configurations in addition to the contributions from anti-site configurations where Fe atoms occupy chain sites. The dangling bonds associated with these sharp features at $E_F$ may also contribute to the observed anomalous vibrational features.

In the previous study of specific heat of Fe$_2$Al$_5$ an anomalous $γ$ (T-linear term) was observed, with a downturn at low temperatures [5]. Sample-dependent values were observed close to $γ = 100$ mJ/mol K$^2$ (adjusted to formula unit = Fe$_2$Al$_{10}$) and this was attributed to anharmonic vibrational modes associated with the disordered structural chains. From the density of states calculated here for Fe$_2$Al$_{10}$ we obtained a density of states at the Fermi level of 14.1 states/eV f.u. Using the standard relation for metallic systems, we obtain $γ = 8.3$ mJ/mol K$^2$. Even with the narrow peak observed in Fe$_2$Al$_{11}$ this value becomes 20 mJ/mol K$^2$. These values are much smaller than fitted from experimental measurements confirming that the main contribution is not due to electrons.

In Fig. 4 the partial density of states for Fe d states is shown, while in the inset the Al s and p states are shown, for Fe$_2$Al$_{10}$. In Fe$_2$Al$_{10}$ the d states have the largest contribution for Fe sites. There are two inequivalent Fe sites but their contributions are practically the same. Also the density of states is practically the same for all three Al sites. From Fig. 4 the large pseudogap due to sp-d hybridization and broad minima in Al s and p states can be clearly seen.

FIGURE 4 HERE

In Fig. 5 (a) and (b) the densities of states for Zn substituted configurations are shown. In the case of Fe$_4$Al$_{10}$Zn$_{0.5}$ the spin down is the majority. The difference between the number spin up and spin down states for this case is 2.34 states/eV f.u., while for Fe$_2$Al$_{10}$Zn the difference is practically zero. From Table I, Fig. 5 (a) and (b) it is clearly observed that the replacement of Fe for Zn in the chains leads to a reduction in spin difference conducting to a reduction in the magnetic moment. Starting with a partial reduction for Fe$_2$Al$_{10}$Zn$_{0.5}$ and becoming completely suppressed when Fe is entirely changed with Zn.

FIGURE 5 HERE
III. CONCLUSIONS

Magnetic properties on Fe-Al and Fe-Al-Zn compounds were investigated by first principles calculations. From the results we observed that the magnetization increases with the increase of Fe content along the partially occupied chains. However there is an intrinsic dilute magnetic contribution corresponding to specific local configurations for Fe, which contributes narrow peaks near the Fermi energy. The Fe replacement on chain sites also induces an enhancement in the density of states at the Fermi level that leads to higher magnetic moments. For the Fe-Al-Zn materials the calculations predict that the full substitution of Zn for Fe in the chain leads to a reduction in the majority spin for partial Zn substitution, and a complete suppression for the Fe$_2$Al$_{10}$Zn configuration.

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REFERENCES


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Fig. 1. Fe$_2$Al$_{10}$ structure.

Fig. 2. Total calculated density of states for spin up and down states in several Fe-Al configurations.
Fig. 3. $d$-partial density of states (non polarized) for one site in the Fe$_4$Al$_{11}$ configuration.

Fig. 4. Partial density of states for Fe$_3$Al$_5$.

Fig. 5. Total calculated density of states for spin up and down states in two distinct Fe-Al-Zn configurations.