Abstract:
We present a detailed structural investigation via neutron diffraction of differently heat treated samples Fe$_{2+x}$VAl and Fe$_{2+x}$V$_{1-x}$Al. Moreover, the magnetic behaviour of these materials is studied by means of $\mu$SR and Mössbauer-experiments. Our structural investigation indicates that quenched Fe$_2$VAl, exhibiting the previously reported “Kondo insulating like” behaviour, is off-stoichiometric (6%) in its Al content. Slowly cooled Fe$_2$VAl is structurally better ordered and stoichiometric, and the microscopic magnetic probes establish long range ferromagnetic order below $T_C = 13K$, consistent with results from bulk experiments. The magnetic state can be modelled as being generated by diluted magnetic ions in a non-magnetic matrix. Quantitatively, the required number of magnetic ions is too large as to be explained by a model of Fe/V site exchange. We discuss the implications of our findings for the ground state properties of Fe$_2$VAl, in particular with respect to the role of crystallographic disorder.

1. Introduction
Recently, the magnetic phase diagram of the alloying series (Fe$_{1-x}$V$_x$)$_3$Al has been the focus of various detailed studies [1,2]. In particular, Heusler-type Fe$_2$VAl has been reported to exhibit a very unusual behaviour for an intermetallic compound, namely a semiconductor-like resistivity close to a magnetic instability [1]. This was interpreted in terms of Kondo-insulating behaviour, analogous to the system FeSi [3,4]. In contrast, optical conductivity studies provided evidence for a pseudogap in the density of states of
Fe$_2$VAl of 0.1-0.2eV [5], a view supported by various band structure calculations [6-8]. Notably, no temperature dependence of the gap features has been detected in these studies, apparently contradicting a Kondo insulator scenario for Fe$_2$VAl. However, the pseudogap scenario itself does not account for the unusual resistivity of Fe$_2$VAl, as in the absence of magnetic correlations it should predict no or a positive metallic magnetoresistance, in conflict with experimental observations [2,9]. Therefore, in Ref. 5 it has been speculated that the (magneto)resistivity of Fe$_2$VAl reflects a mixture of electron excitation processes over the pseudogap and spin dependent scattering from impurities.

Independently, on basis of specific heat and NMR-experiments it has been demonstrated that in Fe$_2$VAl crystallographic disorder, assumed to be present in form of atomic site exchange between Fe and V atoms, substantially affects the ground state properties of this compound [10,11]. In particular, the anomalous low temperature specific heat has been attributed to ferromagnetic clusters with a density of 0.003-0.004/unit cell, consistent with the results from NMR experiments. These works, as well, are in broad agreement with the results from band structure calculations, which predict that via Fe/V site exchange or crystallographic superstructure formation ferromagnetic clusters or long-range order might be generated in Fe$_2$VAl [6-8]. Recently, it has been claimed that such impurity induced ferromagnetism was observed in the related Heusler compound Fe$_2$TiSn [12].

Matsushita and Yamada [13] found that the bulk properties of Fe$_2$VAl exhibit a very strong dependence on the applied heat treatment. They demonstrated that by way of different cooling procedures after an annealing stage the nature of the ground state of Fe$_2$VAl can be tuned: while quenched material exhibits the previously reported semiconducting-like, non-magnetic behaviour [1], a sample slowly cooled down to room temperature after a heat treatment shows almost metallic transport and a ferromagnetic transition at $T_C = 13$K. Specific heat measurements assert the bulk nature of the magnetic transition in the slowly cooled samples.

In this context, the question arises if any or which material – slowly cooled or quenched – Fe$_2$VAl represents the intrinsic behaviour of this compound. Based on the band structure, specific heat and NMR results, it would have to be argued that in slowly cooled material either a crystallographic superstructure has been formed [6] or that a larger level of Fe/V site exchanges is present [7,8], both which might generate long-range magnetic order. Metallurgically, this is counterintuitive, as the slow cooling procedure should
allow the system a more complete relaxation from internal strain and non-equilibrium site occupations, compared to the freezing in of such forms of crystallographic disorder in the quenched material. Further, since ferromagnetism in slowly cooled Fe$_2$VAl is a bulk phenomenon, in the absence of a crystallographic superstructure it requires a drastic increase of the number of Fe/V site exchanged positions from the value in the quenched material, 0.003-0.004/unit cell, probably up to the level of the percolation limit, i.e., $\sim$10-20%, in slowly cooled samples. Such a strong dependence of the number of Fe/V site exchanges on the cooling procedure would require a critical re-examination of previous results on Fe$_2$VAl. Finally, if the resistivity, as suggested in Ref. 5, largely arises from spin dependent scattering, then the very strong reduction of the resistivity in the slowly cooled sample rather indicates a reduction of disorder scattering, in conflict with a view of impurity induced ferromagnetism.

Given this contradictory experimental situation we decided to perform a thorough structural and magnetic investigation of slowly cooled Fe$_2$VAl, concentrating here on microscopic experimental techniques, complementary to the bulk experiments executed so far [13]. In particular, we performed a high resolution neutron diffraction study and Mössbauer spectroscopy on slowly cooled and quenched Fe$_2$VAl. In addition, we performed similar investigations on other samples from the series Fe$_{2+x}$V$_{1-x}$Al, $x > 0$, in order to obtain reference data. Further, we studied slowly cooled Fe$_2$VAl by means of muon spin relaxation. We have chosen these techniques for the following reasons:

a.) If a crystallographic superstructure is formed in slowly cooled Fe$_2$VAl, it should be detectable in diffraction experiments. The contrast between Fe, V and Al in x-ray diffraction, because of similar atomic weights, is weak, and might hinder an observation of a superstructure. Therefore, neutron diffraction experiments are more suitable, as Fe, Al and V have very different neutron scattering lengths yielding a bright contrast (Fe: 9.45·10$^{-15}$m; Al: 3.45·10$^{-15}$m; V: -0.38·10$^{-15}$m). Further, a superstructure might give rise to different local environments resolvable in Mössbauer spectra, that is in form of a double peak spectrum resulting from different isomer shifts at inequivalent lattice sites.

b.) $^{57}$Fe-Mössbauer spectroscopy and muon spin relaxation are used to characterise the magnetic properties microscopically. In addition to long range magnetic order these local probe techniques allow to examine inhomogeneous magnetic states caused by crystallographic disorder. However, the
expected size of the average magnetic moment in Fe$_2$VAI ($\sim 0.1\mu_B$) is at the sensitivity limit of Mössbauer-spectroscopy. Therefore, muon spin relaxation has been used as the most sensitive microscopic method to examine static magnetic order.

c.) If magnetic order stems from a large number ($\sim 10\%$) of Fe/V site exchanged positions, with the bright Fe/V contrast this should be resolved in a neutron diffraction experiment, and possibly in Mössbauer spectroscopy and muon spin relaxation studies.

d.) Repeating similar experiments for a number of samples Fe$_{2+x}$V$_{1-x}$Al, $x > 0$, enables us to compare the results on nominally ordered Fe$_2$VAI to those deliberately containing crystallographic disorder, thus allowing us to assess the relevance of disorder for the magnetic ground state of the systems.

We note that previously Mössbauer experiments have been performed on Fe$_{2+x}$V$_{1-x}$Al, $0.1 \leq x \leq 1$ [14,15]. In these works broad field distributions in the magnetically ordered state have been observed, which however have been interpreted in terms of magnetic fluctuations, in variance with the present view of long-range magnetic order. Further, the magnetic phase diagram determined in Ref. [15] differs greatly from that in [1,16], thus adding to the inconsistencies, and Fe$_2$VAI was not specifically considered in these works.

2.) Experiments and results

a.) Metallurgy: Stoichiometric mixtures of the constituent elements Fe (4N), V (3N) and Al (5N) have been arc-melted in a copper crucible under argon (5N) atmosphere and simultaneous Ti-gettering [13]. The weight loss during this process was less than 0.5\%. The specimens were cut from the polycrystalline ingot and sealed in evacuated quartz ampoules for the heat treatment. Initially, the two samples Fe$_2$VAI were homogenised at 1273K for 24h. The first sample (referred to as ”q-Fe$_2$VAI”) was quenched in water after the heat treatment. The second one (referred to as ”sc-Fe$_2$VAI”) was slowly cooled to 553K at a rate of –6K/h, and subsequently furnace cooled. Other samples Fe$_{2+x}$V$_{1-x}$Al ($x=0.5$, 0.1, 0.02, 0.01) were cooled down to 373K at a rate of –60K/h after homogenisation at 1273K during 15h. Scanning electron microscopy (SEM) pictures have been taken on the samples, indicating that the materials consist of a homogeneous majority phase, with small inclusions of pure Al or Al-oxides.

The samples have been characterised via resistivity and susceptibility, and for Fe$_{2+x}$V$_{1-x}$Al, $x=0.5$, 0.1, 0.02, 0.01 and q-Fe$_2$VAI they exhibit the previously reported behaviour [1,16], with a suppression of magnetic order.
and a tendency towards semiconductivity as \( x = 0 \) is approached. In contrast, sc-Fe\(_2\)VAl has a ferromagnetically ordered ground state and a more metallic resistivity, as reported in Ref. [13]. The transition temperatures, determined from the resistivity experiments, are: \( x = 0.5: T_C > 300K; \) 0.1: \( T_C = 28K \), \( x = 0.02, 0.01 \) and q-Fe\(_2\)VAl: \( T_C < 2K \); sc-Fe\(_2\)VAl: \( T_C = 13K \).

**b.) Neutron scattering results:** The structure of Fe\(_{2+x}\)V\(_{1-x}\)Al, \( 0 \leq x \leq 1 \), derives from the cubic \( DO_3 \) lattice of Fe\(_3\)Al. In this lattice Fe occupies two inequivalent sites (Fig. 1a): Fe I on \((1/2 1/2 1/2)\), and Fe II on \((1/4 1/4 1/4)\) and \((3/4 3/4 3/4)\), respectively. It is assumed that for \( x < 1 \) the V ion almost entirely replaces Fe on the Fe I site [1]. For \( x = 1 \), that is for Fe\(_2\)VAl, this leads to a fully ordered Heusler lattice, with Fe, V and Al each occupying separate cubic sublattices. Band structure calculations [6-8] indicated that in Fe\(_2\)VAl each Fe ion occupying an Fe I site carries a magnetic moment. This requires a site exchange of V with an Fe II ion, which might cause, either via superstructure formation (i.e., V occupying exclusively one Fe II site) or a sufficiently large level of random Fe II/V site exchanges, a magnetically ordered state or anomalous behaviour from diluted magnetic clusters.

In Fig. 1b we plot the calculated neutron diffraction intensities for above three structural modifications of Fe\(_2\)VAl: the fully ordered Heusler lattice, 10\% random Fe II/V site exchange and a superstructure with V entirely occupying one Fe II site. Qualitative and quantitative differences between the calculated spectra are clearly visible, indicating that in a high resolution neutron diffraction experiment the level of Fe II/V site exchanged positions should be resolvable down to about 3\% Fe on V sites.

Powder neutron diffraction data on Fe\(_{2+x}\)V\(_{1-x}\)Al, \( 0 \leq x \leq 0.5 \), have been taken on the Fine-Resolution-Powder-Diffactometer E9 of the Hahn-Meitner-Institute (HMI) in Berlin [17]. The diffractograms have been recorded in the region \( 2\Theta = 5 - 155^\circ \), with an incident neutron wavelength \( \lambda = 1.7964(1)\AA \) at temperatures \( T = 50K \). Full Rietveld structure refinements of the diffraction data were performed employing the program WinPLOTR/FULLPROF [18]. Typical results are presented in Fig. 2, where we plot the data for the sample with nominal composition Fe\(_{2.1}\)V\(_{0.9}\)Al. In the plot we include the refined fit, Bragg peak positions and the difference between fit and data. Spectra of similar high statistics have been taken for both samples (q- and sc-) Fe\(_2\)VAl, and for Fe\(_{2+x}\)V\(_{1-x}\)Al, \( x = 0.02, 0.5 \).

All spectra correspond to the fully ordered cubic \( Fm\overline{3}m \) Heusler structure with some site disorder; a formation of a crystallographic superstructure has not been detected for any sample. In addition, for all samples between one
and five Bragg peaks from an impurity phase, aside from those reflections coming from the \textit{Fm\textbar 3m} lattice, have been observed. In view of the SEM results, the second phase probably is pure Al or Al-oxide; the relative intensity of the corresponding Bragg peaks is low (between 0.3 to 1.3\% for the largest peak), implying a small volume amount of this second phase (about 1\% ). We have tested if the refinements depend upon taking the secondary phase into account, but did not find a significant influence on the results. This reflects that the residual value of $R_{\text{Bragg}}$ is almost completely determined by the mismatch between the fitted profile functions and the experimental data for the Bragg peaks of the cubic \textit{Fm\textbar 3m} phase.

More specifically, to refine our data we used as input the cubic Heusler lattice, but modified it to incorporate different types of disorder: a.) assuming nominal composition; b.) allowing for off-stoichiometry of Fe, V and Al; c.) considering possible site exchange between Fe, V and Al. Consistently, for all samples except for Fe$_{2.5}$V$_{0.5}$Al the closest agreement between refinement and experimental data has been observed for models assuming Al off-stoichiometry. For Fe$_{2.5}$V$_{0.5}$Al the models b.) and c.) did not yield a significantly improved solution compared to a.). Since Fe$_{2.5}$V$_{0.5}$Al is ferromagnetically ordered ($\mu_{\text{ord}} = 0.85\mu_{\text{B}}$), magnetic scattering contributes to the spectrum. Yet, including a ferromagnetic scattering contribution in the refinement did only marginally improve the fit. We stress that we could not find for any of our samples evidence for a significant level ($>3\%$ ) of Fe II/V site exchange.

In Table I we summarise the results of our refinements of the neutron diffraction data on Fe$_{2+x}$V$_{1-x}$Al, $0 \leq x \leq 0.5$. Overall, the refinements yield very good agreement with the experimental data, with $R_{\text{Bragg}}$ values $\sim 2\%$ for $0 \leq x \leq 0.1$. The isotropic thermal displacement parameters $B_{\text{iso}}$, which for V we coupled to that of Al because of the small neutron scattering length of V, exhibit hardly any $x$ dependence. In particular, no significant difference of the $B_{\text{iso}}$ parameters for sc- and q-Fe$_2$VAl has been detected. However, lattice parameters and the measured compositions both show significant differences between the two samples Fe$_2$VAl.

Previously, it has been reported that the lattice parameters of Fe$_{2+x}$V$_{1-x}$Al are decreasing for decreasing $x$ [1]. Specifically, while for $x$ varying from 1 to 0.5 a linear variation of the lattice parameter with $x$ has been found, subsequently a levelling off occurs as $x$ approaches 0, until finally for $x \approx 0$ the lattice expands with $x$. This result is echoed in our experiments: upon reduction of $x$ from 0.5 to 0.02 we observe a non-linear suppression of the lattice parameter $a$ with $x$. This is illustrated in Fig. 3, where we plot the
lattice parameters of Fe$_{2+x}$V$_{1-x}$Al as function of $x$. Remarkably, at $x = 0$, i.e., for Fe$_2$VAl, we find two significantly different values of $a$ for slowly cooled and quenched material: for sc-Fe$_2$VAl it is about 0.02% larger than for q-Fe$_2$VAl. The relevance of this difference is indicated in Fig. 3: the construction with the dashed lines demonstrates that the value of the lattice parameter for sc-Fe$_2$VAl corresponds to that of Fe$_{2.05}$V$_{0.95}$Al. According to the phase diagram from Ref. [16] Fe$_{2.05}$V$_{0.95}$Al is ferromagnetically ordered below $T_C=15$K. Therefore, we argue that the slow cooling procedure causes an expansion of the lattice in sc-Fe$_2$VAl, thus generating negative applied pressure and the onset of ferromagnetic order below $T_C=13$K.

The lattice parameter of q-Fe$_2$VAl falls out of the range of the other, more slowly cooled samples. We believe that this reflects the significant Al off-stoichiometry of this sample. According to our data the actual composition is Fe$_{2}VAl_{0.94(4)}$, well out of the range of nominal stoichiometry. In contrast, for all other samples nominal and actual compositions are identical within experimental uncertainty. More specifically, we directly compare the Bragg spectra measured for sc- and q-Fe$_2$VAl, after normalising them for their overall intensities and correcting the latter for the angular shift from the difference in the lattice parameters. This procedure yields a matching of the positions of the Bragg peaks of sc- and q-Fe$_2$VAl, as demonstrated in Fig. 4 for part of the spectra. We then can directly determine the intensity difference between the two spectra $I_{\text{sc-Fe}_2\text{VAl}} - I_{\text{q-Fe}_2\text{VAl}}$, which is included in Fig. 4. Variations of the intensities for different Bragg peaks are resolvable for the two spectra. We quantify the intensity variations by calculating the relative difference of the areas, \( 1 - \Sigma (I_{\text{q-Fe}_2\text{VAl}}(\Theta) / I_{\text{sc-Fe}_2\text{VAl}}(\Theta)) \Delta \Theta \) under each Bragg peak. In Fig. 5 we present the result of this analysis, with the relative Bragg peak intensities for sc-Fe$_2$VAl in the lower panel, and the intensity variation in the upper one.

The $Fm\bar{3}m$ Heusler lattice consists of four interpenetrating fcc sublattices with origins at $A(0\ 0\ 0)$, $B(1/4\ 1/4\ 1/4)$, $C(1/2\ 1/2\ 1/2)$ and $D(3/4\ 3/4\ 3/4)$. Bragg reflections are produced by either all even or all odd Miller indices with the three structure amplitudes:

\[
F_1 \sim [(f_A - f_C)^2 + (f_B - f_D)^2]^{1/2} \quad \text{for } h,k,l \text{ all odd},
\]
\[
F_2 \sim f_A - f_B + f_C - f_D \quad \text{for } \frac{1}{4}(h+k+l) = 2n+1
\]
\[
F_3 \sim f_A + f_B + f_C + f_D \quad \text{for } \frac{1}{4}(h+k+l) = 2n
\]

with $n$ an integer, and $f_{A,B,C,D}$ as average scattering factors for the atoms $A,C=\text{Fe}$, $B=\text{V}$ and $D=\text{Al}$, respectively. For identical stoichiometry of $I_{\text{sc-Fe}_2\text{VAl}}$ and $I_{\text{q-Fe}_2\text{VAl}}$ no variation of the peak intensities $\frac{1}{4}(h+k+l) = 2n$
is expected. In contrast, experimentally we find for these peaks on average a larger intensity in sc-Fe$_2$VAI than in q-Fe$_2$VAI. This proves that a stoichiometry difference exists between the two samples. Further, for $\frac{1}{2}(h + k + l) = 2n+1$ we find consistently that $I_{sc-Fe_2VAI}<I_{q-Fe_2VAI}$, which in view of the different $F3$ reflects that $f_{D_{q-Fe_2VAI}}<f_{D_{sc-Fe_2VAI}}$, i.e., a smaller Al concentration in the quenched sample compared to sc-Fe$_2$VAI. Because of the comparatively small intensities of peaks $[hkl] = all\ odd$, it yields a large error in the difference $I_{sc-Fe_2VAI}-I_{q-Fe_2VAI}$, prohibiting conclusions on the structural properties from the intensity variations of these peaks.

Refining the neutron spectra assuming stoichiometric composition Fe:V:Al = 2:1:1 yields for sc-Fe$_2$VAI a value $R_{Bragg} = 1.9\%$, which is significantly smaller than that of q-Fe$_2$VAI, $R_{Bragg} = 2.7\%$. Therefore, on basis of our neutron diffraction study of differently heat treated samples Fe$_{2+x}$V$_{1-x}$Al we conclude that sc-Fe$_2$VAI, which is magnetically ordered below $T_C = 13$K, structurally is much better ordered than q-Fe$_2$VAI. Primarily, the disorder in q-Fe$_2$VAI arises from Al vacancies, while Fe/V site exchange is not observable for any sample within the resolution of our experiment.

In addition to our structural investigation we attempted to study the magnetically ordered phases of sc-Fe$_2$VAI and Fe$_{2.1}$V$_{0.9}$Al using the focusing diffractometer E6 at the HMI. We were unable to resolve intensity differences between measurements taken above and below $T_C$ in our powder neutron diffraction experiments, indicating that for both sc-Fe$_2$VAI and Fe$_{2.1}$V$_{0.9}$Al the ground states are ferromagnetically ordered with magnetic moments smaller than the resolution limit at E6 of about 0.5$\mu_B$.

c.) $\mu$SR-experiments: We performed time-differential muon spin relaxation experiments in zero external field (ZF-$\mu$SR) on above powdered specimen of slowly cooled sc-Fe$_2$VAI in the temperature range 3 - 225K at the GPS spectrometer of the Paul Scherrer Institute, Switzerland. The sample was mounted with ultra thin aluminium tape in a gas flow cryostat and an electronic veto logic was used to register only the decay positron signals from muons stopped in the sample.

The muon spin polarisation as a function of time is reconstructed by forming the asymmetry between the numbers of positrons emitted parallel and antiparallel to the original muon spin polarisation direction. As described in [19] the experimentally determined asymmetry $A(t)$ is given as $A(t) = A_0 G(t), where A_0 \sim 0.21$ is the experimentally determined intrinsic asymmetry of the positron detectors and $G(t)$ the normalised polarisation function of the muon ensemble implanted in the sample.
In zero external field a possible source for a relaxation of the muon spin ensemble are static local magnetic fields at the muon site, $B_{\text{loc}}$, due to finite electronic magnetic moments. The individual muon spin shows a Larmor precession around $B_{\text{loc}}$ at a frequency $\omega = \gamma_\mu B_{\text{loc}}$, with $\gamma_\mu/2\pi = 13.55\,\text{MHz/kG}$.

For a magnetically ordered polycrystalline sample an isotropic spatial averaging over all angles between $B_{\text{loc}}$ and the initial muon polarisation $P_\mu(0)$ yields a polarisation function $G(t) = 1/3 + 2/3 \cos(\omega t) \exp(-(\lambda_{\text{stat}} t)^\beta)$ [20]. The relaxation of the oscillating part describes an inhomogeneous distribution of $B_{\text{loc}}$ for the total muon ensemble. If the average value of $B_{\text{loc}}$ is zero and the form of the distribution is Gaussian, $G(t)$ is given by the Kubo-Toyabe function $G(t) = 1/3 + 2/3 (1-\Delta^2 t^2) \exp(-1/2\Delta^2 t^2)$ [20]. In general, a static local field distribution in a polycrystalline sample will always lead to a longitudinal non-relaxing 1/3-tail and a transverse relaxing 2/3-signal fraction. If the field distribution becomes dynamic with a slow fluctuation rate $\nu << (\lambda_{\text{stat}}$ or $\Delta$), the 1/3-tail will exhibit a relaxation $\sim \exp(-\lambda_{\text{long}} t)$. For fast fluctuations ($\nu >> (\lambda_{\text{stat}}$ or $\Delta$)) a single component relaxation function $G(t) = \exp(-(\lambda_{\text{dyn}} t)^\beta)$ can be employed.

Typical ZF-\(\mu\)SR spectra of Fe$_2$VAl are depicted in Fig. 6. At temperatures below 13K a two component structure of a quasi-static spectrum exists: a fast relaxing transversal part of nearly 2/3 total signal amplitude and a slowly relaxing longitudinal part. No oscillating signal fraction is detected. Between 13 and 40K the fast relaxing signal fraction gradually disappears and above 40K only a single, slowly relaxing signal is observed.

The data sets can be described by a phenomenological polarisation function of the form

$$A(t) = A_0 \left( F_{\text{slow}} \exp(-(\lambda_{\text{long}} t)^\alpha) + (1- F_{\text{slow}}) \exp(-(\lambda_{\text{trans}} t)^\beta) \right).$$

Common parameters at all temperatures are the spectrometer asymmetry $A_0 = 0.21$ and the generalised exponents $\alpha = 1.15(2)$ and $\beta = 0.64(3)$ describing the shape of the relaxation functions of the slow and fast components, respectively. The temperature dependence of the relative asymmetry $F_{\text{slow}}$ of the slow component is plotted in Fig. 7, the resulting muon spin relaxation rates $\lambda_{\text{long}}$ and $\lambda_{\text{trans}}$ in Figs. 8 and 9.

The full signal amplitude in the temperature regime above 40K reflects a paramagnetic relaxation of the muon spin. An additional 10% signal amplitude increase between 40 K and higher temperatures is attributed to a change of the experimental set-up (i.e., time resolution). The increase of the relaxation rate with decreasing temperature (Fig. 8) arises from the slowing down of the paramagnetic moments. Between 40 and 12K the amplitude of
this signal is gradually reduced and a strongly relaxing component appears, reflecting a sample volume fraction with quasi-static magnetic moments on a time scale of $\sim 10^{-7}$ s, e.g. inhomogeneous short range magnetic order. The ordered volume fraction continuously increases from zero at $\sim 40$K to 100% at 12K. The $\mu$SR data confirm a magnetic transition between 15 and 12K, since the low temperature value of $F_{\text{slow}} = 0.29(2)$ clearly proves that below 13K the sample is fully magnetically ordered. The 10% deviation of $F_{\text{slow}}$ from the theoretical value 1/3 is due to the constant sample amplitude fixed to the high temperature value above 40K. The reduction of $\lambda_{\text{long}}$ between 40 and 12K reflects the change of the nature of the relaxation mechanism from dynamic in the paramagnetic regime above 40K to a quasi-static one of the longitudinal muon spin component in the magnetically ordered state. The saturation value of $\lambda_{\text{long}} \sim 0.27(2)\mu s^{-1}$ below 12K corresponds in a strong collision model to an effective spin fluctuation rate of the same order. The very strong transversal relaxation rate $\lambda_{\text{trans}}$ in the ordered state and the absence of a coherent muon spin precession indicate a rather inhomogeneous magnetic state with a broad local field distribution at the muon site. The increase of $\lambda_{\text{trans}}$ with decreasing temperature is compatible with the increase of the magnetisation at low temperatures. The value at 20K corresponds to a strongly reduced signal asymmetry in the intermediate regime between paramagnetic and ferromagnetic state and is not directly comparable with those at lower temperatures.

The fitted value of the shape exponent $\alpha$ is close to 1, the expected value for a quasi-static relaxation of the longitudinal signal fraction in the magnetically ordered state. In the paramagnetic regime this value is consistent with a homogeneous relaxation process with a gaussian local field distribution and a well defined spin fluctuation rate. In the ordered state below 13K the exponent $\beta$ is significantly smaller than 1, which is usually observed in inhomogeneous magnets without spontaneous muon spin precession. In Fe$_2$VAI the main sources of the static field distribution are imperfections of the magnetic lattice caused by diluted lattice imperfections and impurities. In this case a lorentzian field distribution (exponent $\beta = 1$) is expected for dominant dipolar or RKKY-type hyperfine coupling between the muon and the local moments [21]. The observed behaviour is an indication for an inhomogeneous magnetic state causing a superposition of more than one lorentzian field distribution with different static widths. The $\mu$SR data cannot unambiguously clarify the cause for this inhomogeneity. Either size and orientation variations of small magnetic moments on each Fe site or diluted moments like in
a spin glass might be possible. Assuming the latter to be the case, we can compare the low temperature saturation value of $\lambda_{\text{trans}} \sim 47(3) \mu s^{-1}$ to that of a canonical spin glass like (Au)Fe [22], where a linear scaling of $\lambda_{\text{trans}}$ with the impurity spin concentration has been observed. From this comparison we obtain an impurity spin concentration of about 8(2)% in sc-Fe$_2$VAl. This value is consistent with the Mössbauer results presented below but incompatible with the upper bound for Fe II/V site exchange from neutron scattering.

d.) Mössbauer-spectroscopy: $^{57}$Fe-Mössbauer-spectroscopy experiments were executed on all samples Fe$_{2+x}$V$_{1-x}$Al, $0 \leq x \leq 0.5$, in a standard low-temperature Mössbauer set-up (source: $^{57}$Co in Rh matrix) at temperatures ranging from 8 to 300K. A full account of our experiments will be presented elsewhere [23]; here, we only address two aspects of our Mössbauer studies on Fe$_{2+x}$V$_{1-x}$Al.

In Fig. 10 we present the Mössbauer spectra of Fe$_{2.1}$V$_{0.9}$Al measured at 50 and 10K, together with the corresponding spectra of sc-Fe$_2$VAl at 50 and 8K. The experiments at 50K probe the paramagnetic state, while at 8/10K the systems are ferromagnetically ordered. For both compounds similar Mössbauer spectra are observed: at 50K we detect single lines with small isomer shifts of about 0.02-0.03mm/s, relative to $^{57}$Co(Rh), and linewidths (FWHM) $\Gamma$ 0.22mm/s (solid lines in Fig. 10). Upon lowering the temperature below $T_C$ a further broadening of the lines and a reduction of their depth occurs. The close quantitative and qualitative similarity between the temperature dependence of the Mössbauer spectra of Fe$_{2.1}$V$_{0.9}$Al and sc-Fe$_2$VAl is emphasised by plotting the difference between the spectra at 50 and 8/10K for both compounds (Fig. 10). It reinforces the notion of ferromagnetism in sc-Fe$_2$VAl as result of the same mechanism as in Fe$_{2.1}$V$_{0.9}$Al and is consistent with our view that it arises from negative chemical pressure.

For both Fe$_{2.1}$V$_{0.9}$Al and sc-Fe$_2$VAl the observed behaviour is not the expected one for an archetypical bulk ferromagnet, since no well-defined Zeeman splitting is visible. Previously, the Mössbauer-spectra of Fe$_{2+x}$V$_{1-x}$Al have been interpreted in terms of fluctuating spins [14,15] and on basis of a "shell model" of magnetic ions immersed in a non-magnetic matrix [9]. The first model is inconsistent with the observation of bulk ferromagnetic ordering for Fe$_{2.1}$V$_{0.9}$Al and sc-Fe$_2$VAl.

The shell model has been successfully applied to disordered metallic ferromagnets like Fe-Al alloys [24]. It assumes that the hyperfine field at a given Fe ion results from a superposition of the contributions of magnetic
ions sited in the nearest neighbour, next-nearest neighbour etc. shell around the Fe ion. In Fe$_{2+x}$V$_{1-x}$Al the magnetic ions are thought to be Fe II on V sites, which on basis of band structure calculations are predicted to carry a large ($2\mu_B$) magnetic moment [6-8]. From our Mössbauer data we can estimate for sc-Fe$_2$VAl the required number of site exchanged Fe II/V pairs: to account for the broadening of the Mössbauer-line below $T_C$ it would require at least 6% Fe II on V sites. This value, which is more than one order of magnitude larger than the estimated level of Fe/V site exchanges for q-Fe$_2$VAl of 0.3-0.4% [10,11], is inconsistent with the result of our neutron diffraction experiments, setting an upper limit of 3% Fe II on V sites. Therefore, we conclude that neither model proposed so far properly accounts for the Mössbauer spectra of Fe$_{2+x}$V$_{1-x}$Al, $x\approx 0$.

3.) Conclusions
We have presented powder neutron diffraction, $\mu$SR and Mössbauer-experiments on Fe$_{2+x}$V$_{1-x}$Al, and in particular on differently heat treated samples Fe$_2$VAl. Our structural investigation proves that slowly-cooled Fe$_2$VAl, which we established on a microscopic scale to be ferromagnetically ordered below $T_C= 13$K, is structurally better ordered than quenched material, for which we found evidence for substantial Al off-stoichiometry. For the quenched material the bulk properties [13] resemble the behaviour of "Kondo-insulating like" or "pseudogap" Fe$_2$VAl [1,2,5,9-11,16]; this suggests that the materials investigated in those works are Al deficient.

As pointed out in Ref. [5], because of the electron count Al deficiency might have a strong effect on the actual position of the Fermi level $E_F$ in a pseudogap system. Specifically, it was argued that Al deficiency moves $E_F$ out of the centre of the pseudogap into the slopes, implying that Al deficient material should be more metallic than non-deficient one. This hypothesis is in conflict with the observation that the resistivity of sc-Fe$_2$VAl is lower than that of q-Fe$_2$VAl, indicating less metallicity and $E_F$ in the centre of the gap for the latter sample.

Another explanation for the smaller resistivity of sc-Fe$_2$VAl might be based upon the ability of Al vacancies to localise conduction electrons. Then, the resistivity of Fe$_2$VAl would depend strongly on disorder induced (i.e., from Al vacancies) localisation of electrons in states close to the gap; with the larger degree of disorder in q-Fe$_2$VAl its resistivity will be larger than that of sc-Fe$_2$VAl. Unfortunately, quantitative predictions are very difficult for this scenario, as it depends both on the actual position of $E_F$ because
of the number of charge carriers from Al, and the strength and number of localising potentials from Al vacancies. In addition, $E_F$ might depend on the lattice parameter, i.e., the chemical pressure, which in turn is a function of the Al stoichiometry.

Altogether, we conclude that the physical properties, in particular the anomalous resistivity, of non-magnetic Fe$_2$VAl are dominated by crystallographic disorder. Kondo-insulating behaviour seems not to play a role; specifically, Fe$_2$VAl can be easily tuned into a ferromagnet, which is not expected for inherently non-magnetic Kondo insulators [25]. Further, we conclude that sc-Fe$_2$VAl is ”more representative” of the intrinsic behaviour of ambient pressure Fe$_2$VAl than quenched material, as it is closer to perfect stoichiometry. Hence, while the closeness to a pseudogap state predicted in band structure calculations [6-8] is found for both sc- and q-Fe$_2$VAl, the prediction of a non-magnetic ground state for stoichiometric, perfectly Heusler-ordered Fe$_2$VAl must still be considered a matter of debate. In particular, we note that, given our Mössbauer- and $\mu$SR-experiments, the simple view of ”Fe on the wrong (V) site” generating magnetism does not account for magnetic order in sc-Fe$_2$VAl, in so far as the measured number of ”wrong sited” Fe is too low.

Since the properties of Fe$_2$VAl are so sensitively dependent on the actual stoichiometry, which is hard to control in the limits relevant to Fe$_2$VAl, we believe that pressure experiments on either sc-Fe$_2$VAl or q-Fe$_2$VAl represent a more fruitful route to study this material. Based on our experiments, for sc-Fe$_2$VAl we would expect a suppression of magnetic order upon application of pressure. For q-Fe$_2$VAl a pressure experiment might yield insight in the relevance of Al vacancies for electronic localisation and the position of the Fermi level. Furthermore, pressure experiments might be very useful in combination with band structure calculations, as we would expect that the result of these calculations should sensitively depend on the value of the lattice constant.

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References:
[1] Nishino Y, Kato M, Asano S, Soda K, Hayasaki M, Mizutani U 1997 Phys. Rev. Lett. 79 1909
[2] Endo K, Matsuda H, Ooiwa K, Iijima M, Goto T, Sato K, Umehara I 1998 *J. Magn. Magn. Mat.* **177-181** 1437

[3] Schlesinger Z, Fisk Z, Zhang H-T, Maple M B, DiTusa J F, Aeppli G 1993 *Phys. Rev. Lett.* **71** 1748;

[4] Schlesinger Z, Fisk Z, Zhang H-T, Maple M B 1997 *Physica B* **237-38** 460

[5] Okamura H, Kawahara J, Namba T, Kimura S, Soda K, Mizutani U, Nishino Y, Kato M, Shimoyama I, Miura H, Fukui K, Nakagawa K, Nakagawa H, Kinoshita T 2000 *Phys. Rev. Lett.* **84** 3674

[6] Guo G Y, Botton G A, Nishino Y 1998 *J. Phys.: Condens. Matter* **10** L119

[7] Singh D J and Mazin I I, 1998 *Phys. Rev. B* **57** 14352

[8] Weht R and Pickett W E 1998 *Phys. Rev. B* **58** 6855

[9] Matsuda H, Endo K, Ooiwa K, Iijima M, Takano Y, Mitamura H, Goto T, Tokiyama M, Arai J 2000 *J. Phys. Soc. Jpn.* **69** 1004

[10] Lue C-S and Ross Jr. J H 1998 *Phys. Rev. B* **58** 9763

[11] Lue C-S, Ross Jr. J H, Chang C F, Yang H D 1999 *Phys. Rev. B* **60** R13941

[12] Slebarski A, Maple M B, Freeman E J, Sirvent C, Tworuszka C, Orzechowska M, Wrona A, Jezierski A, Chiuzbaian S, Neumann M 2000 *Phys. Rev. B* **62** 3296

[13] Matsushita A and Yamada Y 1999 *J. Magn. Magn. Mat.* **196-197** 669

[14] Popiel E S, Tuszynski M, Zarek W, Rendecki T 1989 *J. Less-Common Met.* **146** 127

[15] Popiel E S, Zarek W, Tuszynski M 1989 *Hyperfine Interactions* **51** 981

[16] Kato M, Nishino Y, Mizutani U, Asano S 2000 *J. Phys.: Condens. Matter* **12** 1769

[17] Többens D M, Stüßer N, Knorr K, Mayer H M, Lampert G, Proc. of the 7. European Powder Diffraction Conference EPDIC 2000

[18] Rodriguez-Carvajal J, Laboratoire Leon Brillouin – CEA-CNRS, Version 3.5d Oct98-LLB-JRC

[19] Nachumi B, Fudamoto Y, Keren A, Kojima K M, Larkin M, Luke G M, Merrin J, Tchernyshyov O, Uemura Y J, Ichikawa N, Goto M, Takagi H, Uchida S, Crawford M K, McCarron E M, MacLaughlin D E, Heffner R H 1998 *Phys. Rev. B* **58** 8760
Fig. 1: a.) The cubic $DO_3$ lattice of Fe$_3$Al, with the two inequivalent Fe sites at Fe I: $(1/2 \ 1/2 \ 1/2)$ and Fe II: $(1/4 \ 1/4 \ 1/4);(3/4 \ 3/4 \ 3/4)$. b.) The calculated normalised neutron diffraction intensities for the three different structural modifications Fe$_2$VAl: the fully ordered Heusler lattice (V on Fe I site), 10% Fe II/V site exchange and V entirely occupying one Fe II site, giving rise to a superstructure.

Fig. 2: The neutron diffraction spectrum of Fe$_{2.1}$V$_{0.9}$Al, measured at 50K (+). Included is a refined fit to the data, the difference between fit and data, and tics indicating Bragg peak positions.

Fig. 3: The lattice parameters of different samples Fe$_{2+x}$V$_{1-x}$Al, 0 $\leq$ x $\leq$ 0.1, as function of x. The inset depicts the data for 0 $\leq$ x $\leq$.5. Lines are guides to the eye.

Fig. 4: The normalised neutron spectra of sc- (solid line) and q-Fe$_2$VAl (+), and the difference $I_{sc-Fe_2VAl}$-$I_{q-Fe_2VAl}$ between the two spectra.

Fig. 5: The relative Bragg peak intensities of sc-Fe$_2$VAl and the intensity variations, calculated from $1 - \Sigma (I_{q-Fe_2VAl}(\Theta) / I_{sc-Fe_2VAl}(\Theta))\Delta\Theta$.

Fig. 6: Zero field $\mu$SR spectra of sc-Fe$_2$VAl at different temperatures. The fit functions (solid lines) are described in the text.

Fig. 7: Temperature dependence of the slowly relaxing signal fraction $F_{slow}$ in zero field $\mu$SR of sc-Fe$_2$VAl.

Fig. 8: Temperature dependence of the longitudinal muon spin relaxation rate $\lambda_{long}$ in zero field $\mu$SR of sc-Fe$_2$VAl.
| Sample          | Lattice parameter a (Å) | $B_{iso-Fe}$ (Å²) | $B_{iso-V/Al}$ (Å²) | Measured composition   | $R_{Bragg}$ |
|-----------------|-------------------------|-------------------|---------------------|------------------------|-------------|
| $Fe_{2.5}V_{0.5}Al$ | 5.7604(3)               | 0.15(8)           | 0.9(2)              | $Fe_{2.5}V_{0.5}Al$    | 4.3 %       |
| $Fe_{2.1}V_{0.9}Al$ | 5.7528(2)               | 0.15(6)           | 0.3(2)              | $Fe_{2.1}V_{0.9}Al_{1.01(5)}$ | 2.0 %       |
| $Fe_{2.02}V_{0.98}Al$ | 5.7521(2)              | 0.13(6)           | 0.4(2)              | $Fe_{2.02}V_{0.98}Al_{1.01(4)}$ | 2.1 %       |
| sc-$Fe_{2}VAl$   | 5.7523(2)               | 0.25(6)           | 0.4(3)              | sc-$Fe_{2}VAl_{0.99(4)}$ | 1.9 %       |
| q-$Fe_{2}VAl$    | 5.7514(2)               | 0.23(6)           | 0.3(3)              | q-$Fe_{2}VAl_{0.94(4)}$ | 2.3 %       |

Fig. 9: Temperature dependence of the transversal muon spin relaxation rate $\lambda_{trans}$ in zero field $\mu$SR of sc-$Fe_{2}VAI$.

Fig. 10: Mössbauer-transmission-spectra of $Fe_{2.1}V_{0.9}Al$ and sc-$Fe_{2}VAl$ taken at 50 (+) and 10/8K ($\circ$). Solid lines indicate single lorentzian fits to the 50K data. Included in the plot are the differences between the spectra at 50 and 10/8K ($\circ$, respectively.

Tables
Table 1: Summary of the refinement results of the neutron diffraction data on $Fe_{2+x}V_{1-x}Al$, $0 \leq x \leq 0.5$, with the cubic lattice parameter $a$, the isotropic thermal displacement parameters $B_{iso}$ of Fe and V/Al, the measured composition and the value of $R_{Bragg}$. 

16
Fe$_{2.1}$V$_{0.9}$Al

$Fm3m$

$a = 5$

$R_{Brag}$
Fig. 5

\[ \Sigma_{hkl} = 2n \]

\[ \Sigma_{hkl} = 2n + 1 \]

Bragg peak \([hkl]\)

- \([111]\)
- \([200]\)
- \([220]\)
- \([311]\)
- \([222]\)
- \([400]\)
- \([331]\)
- \([420]\)
- \([422]\)
- \([511]/[333]\)
- \([440]\)
- \([531]\)
- \([600]\)
\[ \lambda_{\text{long}} \text{ (MHz)} \]

\[ T \text{ (K)} \]

The graph shows the variation of \( \lambda_{\text{long}} \) with temperature \( T \).
Fig. 10

Relative Transmission (%)

Fe$_{2.1}$V$_{0.9}$Al

- T=50K
- T=10K
- diff: 50K-10K

sc-Fe$_2$VAl

- T=50K
- T=8K
- diff: 50K-8K

Velocity (mm/s)