Journal of Alloys and Compounds 663 (2016) 77–81

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

An AC magnetic susceptibility study of a sigma-phase $Fe_{65.9}V_{34.1}$ alloy

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ARTICLE INFO

Article history:
Received 22 September 2015
Received in revised form
3 November 2015
Accepted 7 November 2015
Available online 11 November 2015

Keywords:
Fe–V alloy
Sigma-phase
AC magnetic susceptibility
Reentrant magnetism

ABSTRACT

A sigma-phase $Fe_{65.9}V_{34.1}$ alloy was investigated with the AC magnetic susceptibility as a function of temperature, frequency and external magnetic field. Evidence was found that its magnetism shows features characteristic of a reentrant behavior viz. two transitions: first at T_C ~312 K from the paramagnetic state into a collinear ferromagnetic one, and second at T_f ~302 K to a mixed state (sometimes referred to as a ferromagnetic or re-entrant spin glass) which, finally, at a lower temperature (T_{RSG} ~60 K) transforms to a state where replica symmetry is broken. The frequency dependence of T_f is lower than that of canonical spin glasses, a feature that in the light of a high concentration of magnetic carriers can be understood in terms of a weak coupling between magnetic clusters.

1. Introduction

The Sigma (σ) phase is a member of the Frank–Kasper (FK) family of phases also known as topologically close-packed (TCP) ones, their characteristic feature being high values (12–16) of coordination numbers [1]. An interest in σ (and other FK-phases) has both practical as well as scientific reasons. The former follows from the fact that σ may precipitate in technologically important materials (steels) that – due to their excellent properties – have been used as construction materials in various branches of industry e.g. chemical, petrochemical, traditional and nuclear power plants etc. [2]. Once precipitated, it drastically deteriorates the mechanical properties as well as decreases the corrosion resistance. Consequently, the interest in σ from the practical viewpoint is rather limited to a development of such steels in which the formation of this phase does not occur or, at least, is retarded. In turn, the scientific interest in σ follows from its complex crystallographic structure (a tetragonal unit cell with 30 atoms distributed over 5 non-equivalent sub-lattices) that is attractive in its own right and the fact that interesting physical properties that can be tailored by changing constituting elements and chemical composition (σ has not a definite stoichiometric composition). Concerning the magnetic properties of the σ-phase in binary alloys, the subject of the present study, only σ in Fe–Cr and Fe–V systems are known to be magnetic, and their magnetism was regarded as ferromagnetic [3,4]. Recently, the magnetism in the two systems has been shown to be more complex, viz. it was found to be constituted by a spin glass (SG) of a re-entrant character [5]. Additionally the magnetism of σ was discovered in Fe–Re [6] and in Fe–Mo [7,8] systems with SG being the ground state. The Fe–V system is especially interesting with regard to σ, as the phase can be formed within a wide range of composition, namely for ~33–~65 at% V [9]. This gives a unique opportunity to change the physical properties of σ. Concerning the magnetic ones, the magnetic ordering temperature (Curie point), T_C, can be continuously raised up above room temperature. The actual record obtained for the σ-$Fe_{65.6}V_{34.4}$ alloy is as high as ~307 K as determined from magnetization measurements or ~324 K as found from the temperature dependence of the average hyperfine field [10]. In this paper we report results obtained with AC magnetic susceptibility techniques on a σ-$Fe_{65.9}V_{34.1}$ sample.

2. Experimental

2.1. Sample preparation and characterization

A master alloy of a nominal composition $Fe_{66.5}V_{33.5}$ was prepared by the arc melting of appropriate amounts of elemental Fe (3 N + purity) and V (4 N purity). The melting process was carried out in a protective atmosphere of pure argon and an ingot was flipped and re-melted three times to increase its homogeneity. The ingot was then solution treated at 1273 K for 72 h followed by a

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http://dx.doi.org/10.1016/j.jallcom.2015.11.054
0925-8388/

quenching onto a block of brass kept at 295 K. The transformation of the obtained master alloy into σ was performed by an isothermal annealing of the former in vacuum at 973 K for 25 days followed by quenching. The obtained sample was then powdered and an X-ray diffraction (XRD) pattern was recorded at room temperature as shown in Fig. 1. An analysis with the program FullProf revealed that the original α-phase was transformed into σ to 97.5% with a residual (2.5%) amount of Fe. Consequently, the stoichiometry of σ was $Fe_{59.9}V_{34.1}$. Details of the analysis are given elsewhere [11].

2.2. Magnetic susceptibility measurements

AC magnetic susceptibility (χ_{AC}) measurements were carried out by means of an MPMS SQUID magnetometer. The sample was in the form of a powder and it had a mass of 25.6 mg. Both real (χ') and imaginary (χ'') components of $\chi_{AC} = \chi' - i\chi''$ were registered as a function of increasing temperature (T) in the range of 4–350 K. An oscillating magnetic field from 1 Hz up to 1000 Hz was used and the dependence of the output signal on the amplitude of the driving field (1 Oe and 2 Oe) was tested. The influence of the applied DC magnetic field (H_{DC}) on the temperature behavior of χ_{AC} was investigated for H_{DC} = 100, 200, 500 and 1000 Oe.

The temperature dependence of magnetization was measured in a constant field of 10 Oe in the ZFC and FC regimes by means of a PPMS instrument.

3. Results and discussion

3.1. AC susceptibility in zero magnetic field

3.1.1. The maximum (cusp)

Real (in phase), χ', and imaginary (out of phase), χ'', AC magnetic susceptibility components, measured as a function of temperature, *T*, and frequency, *f*, are shown in Fig. 2. The imaginary component amounts to ~3% of the real one, which points to rather weak. relaxation effects in the studied alloy. Concerning χ', its shape is not typical of classical spin glasses (SGs), like for example *Cu*Mn, for which cone-like curves with concave slopes and a well-defined cusp were observed [12]. It should, however, be noted that the typical shape of χ' was also measured for systems with a high concentration of magnetic carriers and complex crystallographic structures e.g. for a $Tb_{117}Fe_{52}Ge_{113.8(1)}$ compound showing a cluster

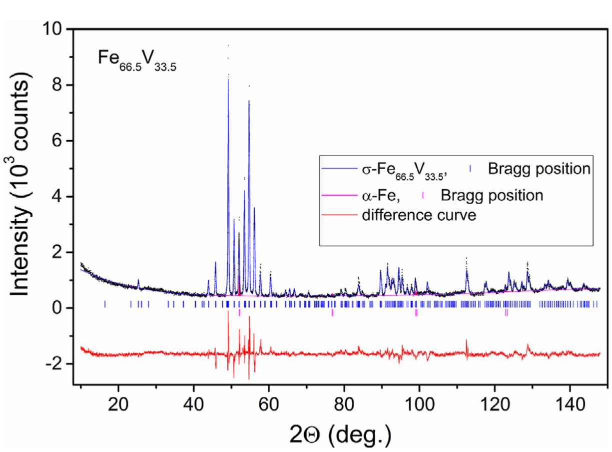

Fig. 1. The Rietveld refinement XRD pattern of the studied $Fe_{66.5}V_{33.5}$ sample recorded at room temperature. Positions of the peaks of the α and σ phases are indicated by vertical bars in black and red, respectively. A difference pattern is also displayed. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

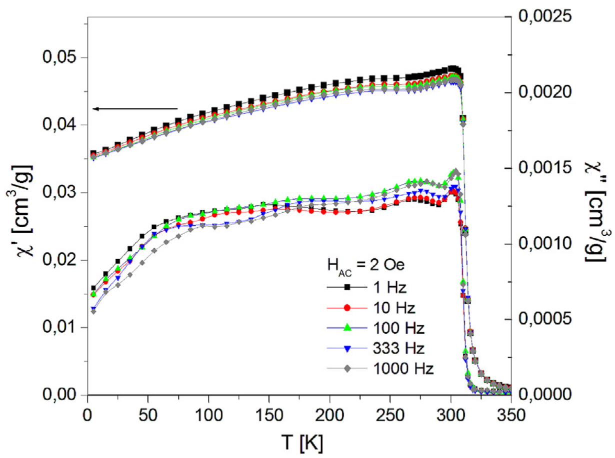

Fig. 2. Real, χ', and imaginary, χ'', components of the AC magnetic susceptibility for the investigated sample versus temperature for the different frequencies indicated.

SG behavior [13], or for σ-Fe_xMo_{100-x} alloys exhibiting several features characteristic of the canonical SGs despite high content of Fe viz. $43 \le x \le 53$ [7]. In contrast to χ', the χ'' data are less regular. In our opinion the interlacement of the χ'' curves, measured with different frequencies of the driving field, arises from the dissimilar anisotropies, hence relaxation, times of particular magnetic sub lattices.

Our preliminary measurement of magnetization according to a field-cooled (FC) and zero-field-cooled (ZFC) protocols are shown in Fig. 3. For AC and DC measurements samples from the same batch but of the different masses were used. Fig. 3a clearly shows that the magnetization of the sample is irreversible. Moreover, the shape of the ZFC curve is virtually the same as that of χ' (see Fig. 3b), as occurs for soft magnetic materials. The ZFC-FC irreversibility is one of the characteristic features of different types of SGs, yet it is not unique to SGs.

In order to shed more light on the nature of the irreversibility we have analyzed the frequency dependence of characteristic temperatures in χ' and χ'' curves in Fig. 2. The most characteristic temperature, known as the spin freezing temperature, T_f, is the one at which the AC susceptibility has its maximum (cusp). Fig. 2 shows evidence that this is the case both for χ' and χ''. For spin glasses and superparamagnets (SPM) both the position of the maximum as well as its height depend on frequency, *f*. The former shifts towards higher temperature and the latter decreases. The shift of T_f, ΔT_f, has been used to distinguish between SGs and SPMs. For this purpose the following figure of merit has been applied:

$$RST = \frac{\Delta T_f / T_f}{\Delta \log f} \quad (1)$$

For SPMs the position of the cusp is more sensitive to frequency, hence the values of *RTS* are significantly higher than those for SGs. However, there is not a well-defined border value of *RTS* between the two systems. As a rule of thumb, $RST \ge$ ~0.2 is indicative of SPMs [14]. SGs can be further divided into two categories viz. canonical (paradigmatic, classical) ones like e.g. *Au*Mn, *Ag*Mn, *Au*Fe, *Cu*Mn for which $RTS \le 0.08$ and cluster SGs e.g. with $0.08 \le RST \le 0.2$ [14]. Also here the border value of *RST* is not sharply defined, hence the classification into the two categories is not fully objective.

A presentation of T_f data in terms of Eq. (1) obtained from χ' curves for H_{AC} = 1 Oe and 2 Oe is shown in Fig. 4. The dependence of T_f on log*f* determined for the χ'' data was not linear for both H_{AC} values used.

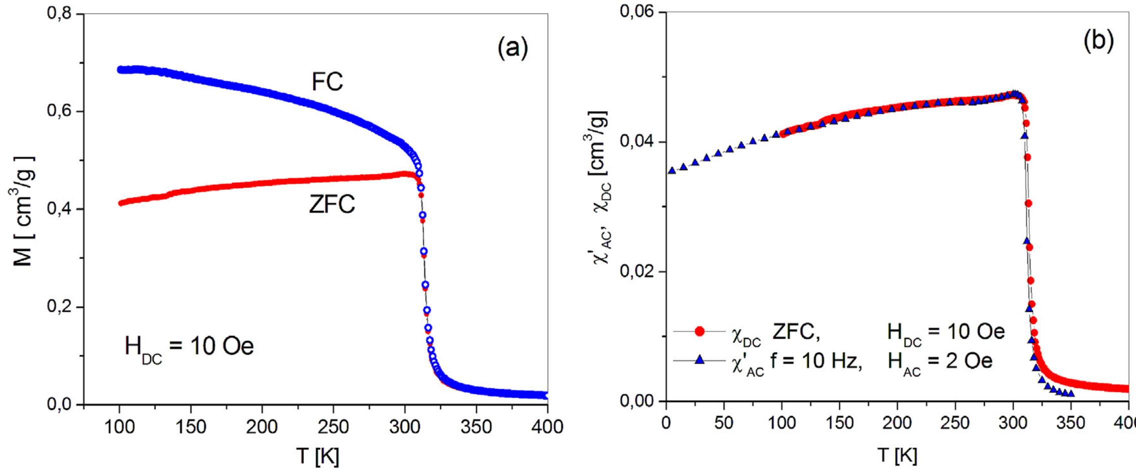

Fig. 3. (a) Temperature dependence of the magnetization of the studied sample in zero-field-cooled (ZFC) and field-cooled (FC) regimes. (b) Direct comparison of AC and DC susceptibilities.

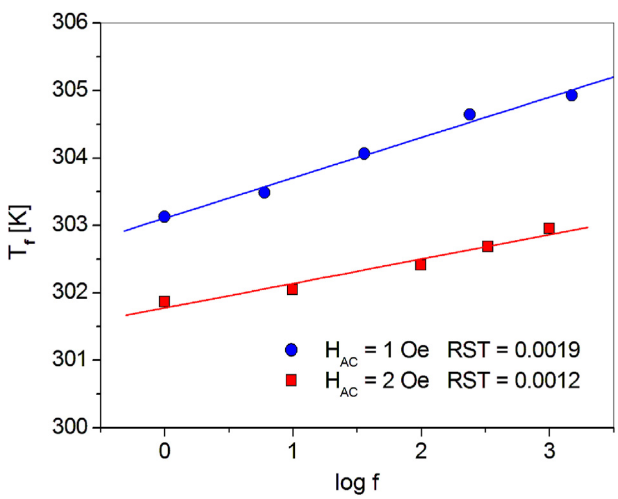

Fig. 4. Relationship between the T_f and logf for measurements carried out at two AC fields (1 and 2 Oe). The solid lines represent the linear fits in terms of Eq. (1).

The derived *RST*-values slightly depend on the amplitude of the AC field, and are equal to 0.0019 and 0.0012 for $H_{AC} = 1$ Oe and 2 Oe respectively. Such values are very small and even smaller than those found for the canonical SGs e. g. 005 for *Cu*Mn [12]. In terms of the above-given criterion, this means that spin glass features are only weakly manifested in the σ-$Fe_{65.9}V_{34.1}$ alloy. With reference to the mean-field theory of SGs, it testifies to very long-range interactions between magnetic entities in the sample. Noteworthy, no shift of T_f has been recently observed for a σ-phase $Fe_{54}Cr_{46}$ alloy [15] and that for σ-FeMo alloys was in the range of 0.0122–0.0135 [7].

Another question relevant to SGs is a description of the frequency dependence of the temperature of the maximum in the AC susceptibility, T_f. Three phenomenological laws can be applied in relation to this question: Arrhenius law – Eq. (2), Vogel–Fulcher law – Eq. (3) and the critical slowing-down law – Eq. (4).

$$f = f_o \exp\left(-\frac{E_a}{k_B T_f}\right) \tag{2}$$

$$f = f_0^{VF} \exp\left(-\frac{E_a}{k_B\left(T_f - T_0^{VF}\right)}\right) \tag{3}$$

$$f = f_o\left(\frac{T_f}{T_{SG}} - 1\right)^{z\nu} \tag{4}$$

Here k_B is the Boltzmann constant, E_a activation energy, T_o^{VF} the Vogel–Fulcher parameter, T_{SG} a spin-glass temperature, and $z\nu$ is known as the dynamic exponent.

Application of Eq. (2) resulted in non-physical values of fit parameters, in particular $f_o = 10^{648}$ Hz and $E_a = 1496$ k_BK. Such values cannot be regarded as physically meaningful. Interestingly, the application of the Arrhenius law to the *Cu*Mn system (Mn content less than ~6 at%) yielded non-physical values for E_a and f_o, as well [12]. On the other hand, in our case the Vogel–Fulcher law yielded reasonable values of the parameters viz. $f_o^{VF} = 2 \cdot 10^{11}$ Hz, $E_a/k_B = 101$ K, $T_o^{VF} = 298$ K. Finally, by using the critical slowing-down law we obtained $T_{SG} = 300.8$ K and $z\nu = 8.5$ which also looks correct.

The parameters obtained from the Vogel–Fulcher law have been used, via the Tholence criterion, to make a distinction between canonical and cluster SGs [16,17]. For this purpose one calculates the following quantity:

$$\delta T_f = \frac{T_f - T_o^{VF}}{T_f} \tag{5}$$

which in our case equals 0.013, a value typical of the canonical SGs. For example $\delta T_f = 0.07$ was found for *Cu*Mn [18]. In terms of an interaction between spin clusters that may exist in our sample due to a high Fe content such a small value of δT_f as 0.013 may also be interpreted as an indication of a very low degree of coupling between the clusters. As an alternative measure of the interactions between spin carriers freezing at T_f, hence the degree of magnetic clustering, we have used the ratio between the activation energy, E_a, and the Vogel–Fucher parameter T_o^{VF} [19]. For the canonical SGs $E_a/k_B T_o^{VF} = 2$–3, whereas for cluster SGs the ratio should be much higher e. g. a value of 30 was reported for *LaAl*$_2$Gd [19]. In the present case the ratio is equal to 0.34, which again supports a very weak coupling between the magnetic clusters if they exist. The latter is plausible despite the high concentration of magnetic Fe

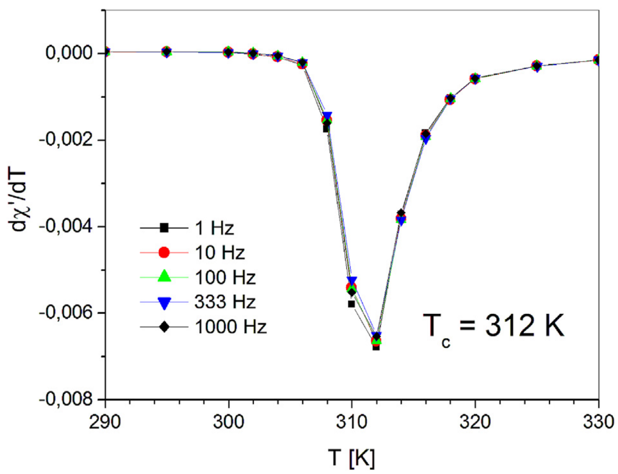

Fig. 5. dχ′/dT versus temperature in the temperature range where χ′ shows the fastest change. The minimum defines T_C.

atoms because the magnetism of σ-phase alloys is highly itinerant [6], hence the magnetic interactions have a very long-range via the inter-cluster magnetic coupling. On the other hand, the common interpretation of a non-zero value of T_0^{VF} as an indication of the existence of magnetic clusters and, via the Tholence criterion, as a measure of inter-cluster interactions, may be put in doubt in the light of its "successful" application to "truly" canonical SGs like e. g. *Cu*Mn [12]. Clusters should be absent in such SGs due to the low concentration of magnetic carriers (below ~6 at%). In such circumstances the frequency dependence of the spin-freezing temperature should be in line with the Arrhenius not with the Vogel–Fulcher law. However, the opposite was found to be true [12].

3.1.2. The magnetic ordering temperature

Previous experimental studies demonstrated that σ-$Fe_{100-x}V_x$ alloys order ferromagnetically [3,10]. The Curie temperature, T_C, strongly depends on the alloy composition ranging between ~15 K for $x = 55$ and ~315 K for $x = 34.5$ (in both cases the average of the values determined from the Mössbauer spectroscopic and DC magnetization measurements are given) [10]. In the light of these results it is reasonable to assume that also the presently studied sample orders ferromagnetically. Based on the previously found relationship between T_C and x [10], we can expect that the value of T_C for the σ-$Fe_{65.9}V_{34.1}$ sample is the highest. We determined it here as the temperature of the inflection point in the χ′(T) curves measured in a low magnetic field (2 Oe) in different frequencies (1–1000 Hz). Data presented in Fig. 5 indicates that the such-determined $T_C \approx 312$ K is frequency independent and testifies to a true phase transition. It should be added that in the case of the σ-$Fe_{65.9}V_{34.1}$ sample $T_C \approx 307$ K was determined from the inflection point in the magnetization curve [10], so the presently found value is the highest one, and, in fact, is in line with the trend revealed for other compositions [10].

3.2. AC susceptibility in a biasing DC magnetic field

An external magnetic field is known for its profound effect on the AC susceptibility of SGs. Especially sensitive is the temperature region in the vicinity of T_f, a feature that was already revealed in the early days of SGs [20]. So it is of interest to investigate such an effect to further explore SGs. As illustrated in Figs. 6 and 7, our measurements are in line with the above-mentioned statement. Concerning χ′, in rather small fields (100 and 200 Oe) the characteristic cusp at T_f has been severely rounded and shifted towards lower temperatures while in stronger fields (500 and 1000 Oe) a significant suppression can be observed accompanied by an appearance of a small peak in the vicinity of T_f. Its exact position is situated at ~313 K and ~315 K for $H_{DC} = 500$ and 1000 Oe, respectively, hence close to the Curie temperature of ~312 K as determined from the inflection point in χ′ measured in zero DC field. A similar behavior of χ′ was observed in some other systems showing reentrant SGs e. g. in NiCoMnSb Heusler alloys [21], and, interestingly, in the ferromagnetic gadolinium [22], the disordered Cr_3Fe ferromagnet [23] or in the layered 2D Heisenberg magnet [24]. Such an anomaly has been explained in terms of short range fluctuations close to the order transition. Regarding the rounded part of χ′ there is a striking difference between the curves recorded in the fields of 100 and 200 Oe and those measured at 500 and 1000 Oe. Namely, in the former ones one observes its downward inclination in the low temperature range. However, the temperature at which this trend begins cannot be precisely defined. It is likely to be related with a transition into a SG "phase" where the transverse components of spins are frozen and replica symmetry is spontaneously broken [25]. The existence of such a transition located at ~60 K, known as

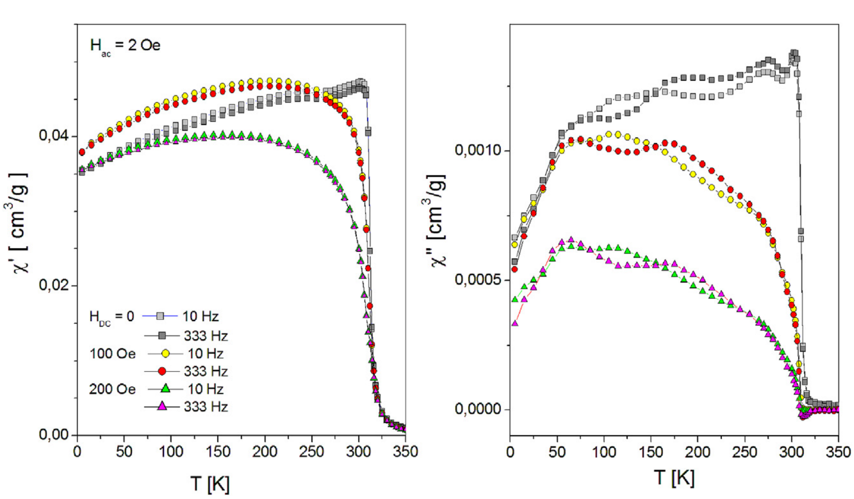

Fig. 6. Real, χ′, and imaginary, χ″, parts of the AC susceptibility versus temperature, recorded for the $Fe_{66.5}V_{33.5}$ sample in biasing DC magnetic fields of 100 Oe and 200 Oe for $H_{ac} = 2$ Oe and two frequencies shown. Data obtained in zero bias field are added for comparison.

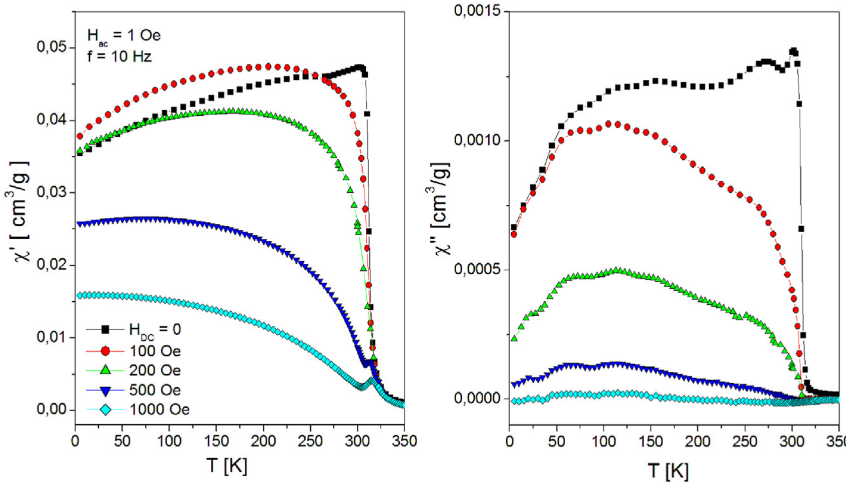

Fig. 7. The effect of a biasing DC magnetic field in the range 100–1000 Oe on χ' and χ'' for the investigated $Fe_{66.5}V_{33.5}$ sample measured at H_{ac} = 1Oe and f = 10 Hz.

the re-entrant temperature, T_{RSG}, can be better seen in the χ'' curves – Fig. 6 where a steep decrease of χ" occurs for T <~60 K. The latter can be taken as an indication of a strong departure from the collinear structure, and strong irreversibility phenomena in the related state.

4. Summary

AC magnetic susceptibility measurements versus temperature (4–350 K), frequency (1–1000 Hz) and external magnetic field (100–1000 Oe) were carried out on a sigma-phase $Fe_{65.9}V_{34.1}$ alloy. They revealed that the magnetism of the investigated sample has a reentrant character: at ~312 K the ferromagnetic order sets in, and at ~302 K there is a transition into a spin-glass-like state which apparently is mixed i.e. the spin glass coexists with the ferromagnetic ordering. At a still lower temperature viz. ~60 K a transition into the ground state was found. This scenario seems to be in line with the mean-field model introduced by Gabay and Thoulouse [25]. Interestingly all figures of merit used to characterize the SG state in the present case like the Tholence criterion, the shift of the spin-freezing temperature per decade of frequency and the ratio between the activation energy and the Vogel–Fulcher temperature have values lower than these for canonical spin glasses. This implies that a magnetic coupling between spin clusters, whose existence in the investigated system is likely to be due to the high concentration of Fe, is very weak. The weakness of the coupling may result from the itinerant character of magnetism observed in the σ-phase systems, as long-range magnetic interactions are expected to diffuse inter cluster interactions.

Acknowledgment

J. Żukrowski is thanked for making the master alloy, J. Przewoźnik for the XRD analysis, and, last but not least, J. M. Williams for improving the language.

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