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C. Pappa, J. Hammann, C. Jacoboni. Spin-glass critical behaviour in the non-dilute disordered insulator CsNiFeF6. *Journal de Physique*, 1985, 46 (4), pp.637-648. 10.1051/jphys:01985004604063700 . jpa-00210004

HAL Id: jpa-00210004

<https://hal.science/jpa-00210004>

Submitted on 1 Jan 1985

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Classification

Physics Abstracts

64.70 — 75.50 — 75.30K

Spin-glass critical behaviour in the non-dilute disordered insulator CsNiFeF₆

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(Reçu le 14 septembre 1984, révisé le 13 novembre, accepté le 30 novembre 1984)

Résumé. — L'analyse de l'aimantation à l'équilibre indique l'existence d'une transition de phase verre de spin à $T_g = 5,37$ K dans le composé isolant non dilué CsNiFeF₆. Une fonction d'échelle a pu être définie, sous la forme $\chi_s = \tau^\beta F(h^2/\tau^{\beta+\gamma})$ avec $\tau = |T - T_g|/T$ et $h = (H + J_0 M)/T$. Les valeurs de β et γ sont : $\beta = 1,2 \pm 0,1$ et $\gamma = 3 \pm 0,5$. Par rapport aux fonctions d'échelle classiques, deux adaptations ont été introduites, permettant l'extension de l'analyse au domaine $T < T_g$ et tenant compte de la valeur non nulle de J_0 :

— le paramètre χ_s correspond en dessous de T_g au paramètre d'ordre q tel qu'il est défini dans le modèle de brisure de la symétrie des répliques développé par Parisi ;

— la variable réduite figurant dans la fonction d'échelle dépend du champ local moyen $H + J_0 M$.

Abstract. — Analysis of field cooled magnetization data in the non-dilute disordered insulator CsNiFeF₆ strongly supports the existence of a spin glass phase transition at $T_g = 5.37$ K. A universal scaling function could be defined above and below T_g . It is written as $\chi_s = \tau^\beta F(h^2/\tau^{\beta+\gamma})$ where $\tau = |T - T_g|/T$ and $h = (H + J_0 M)/T$. The values of β and γ are : $\beta = 1.2 \pm 0.1$, $\gamma = 3 \pm 0.5$. Two accommodations to the usual scaling relation had to be brought in to account for the temperature range $T < T_g$ and for a non-zero value of J_0 :

— the parameter χ_s to be scaled corresponds below T_g to the order parameter q as defined in the Parisi scheme of replica-symmetry breaking ;

— the reduced parameter in the scaling function depends on the mean local field.

1. Introduction.

The question whether spin glasses present a thermodynamic phase transition or not is still very controversial. The dynamic properties of these systems, such as the frequency dependence of the maximum of the a.c. susceptibility, can be explained with phenomenological models, which assume the progressive freezing of the resulting moments of superparamagnetic clusters in the vicinity of T_g . However, the static properties of spin glasses are in qualitative agreement with the results of the mean field theory which predicts the existence of a true phase transition.

If the freezing temperature T_g is a transition temperature and the spin glass a thermodynamically

stable phase, then an associated critical behaviour is expected in the non-linear part (χ_s) of the equilibrium susceptibility, but not in the linear one (χ_0) as for ferromagnets. χ_s is defined as :

$$\chi_s = T \left(\chi_0 - \frac{M}{H} \right). \quad (1)$$

This property is related to the nature of the spin glass order parameter, which in the paramagnetic region ($T \geq T_g$) is equal to the quantity first introduced by Edwards and Anderson [1] :

$$q_{E.A.} = \frac{1}{N} \sum_i [\langle S_i \rangle^2]_{av}. \quad (2)$$

This parameter has the dimensions of the square of the magnetization, so the conjugate field is expected to have the dimensions of the square of a magnetic

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field. According to Chalupa [2], the conjugate field to $q_{E.A.}$ is the square of the width of the internal field distribution ($\tilde{H}^2$) and the spin glass susceptibility $\delta q / \delta \tilde{H}^2$ diverges at T_g as the second derivative of the susceptibility with respect to the conventional uniform field $\delta^2 \chi / \delta H^2$.

Therefore, the critical exponent γ can be determined from the divergence of the non-linear part of the susceptibility at $T > T_g$. Similarly, the critical exponent δ can be derived from the variation of χ_s at T_g as a function of the uniform field [3] :

$$\begin{aligned} T > T_g \quad q &\sim \tau^{-\gamma} \tilde{H}^2 \quad \chi_s \sim \tau^{-\gamma} H^2 \quad (a) \\ T = T_g \quad q &\sim \tilde{H}^{2/\delta} \quad \chi_s \sim H^{2/\delta} \quad (b) \end{aligned} \quad (3)$$

where τ is the usual reduced temperature $\tau = \frac{T - T_g}{T_g}$.

The equivalence between the critical behaviour of q versus $\tilde{H}^2$ and χ_s versus H^2 has also been suggested by Suzuki [4]. Generalizing the equivalence, spin glass scaling functions have been written for $T \geq T_g$ as :

$$\begin{aligned} T \geq T_g \quad \chi_s &= \tau^\beta F_1\left(\frac{H^2}{\tau^{\beta+\gamma}}\right) \quad (a) \\ \chi_s &= H^{2/\delta} F_2\left(\frac{H^{2-2/\delta}}{\tau^\gamma}\right) \quad (b) \end{aligned} \quad (4)$$

As pointed out by Toulouse [5], the results of the mean field theory with infinite range interactions [6] (Sherrington-Kirkpatrick model) are in principle correct in the paramagnetic region i.e. above the de Almeida-Thouless line [7]. This model assumes a Gaussian distribution for the magnetic interactions, the mean value and the width of this distribution being equal to J_0 and J respectively. For $J_0 = 0$ an expansion of the Sherrington-Kirkpatrick (S-K) self consistent equations for the magnetization and $q_{E.A.}$ leads to the relation (the modulus of the spins is assumed to be equal to 1).

$$\begin{aligned} T > T_g \quad M &= \frac{H}{T} - \frac{a_3}{T^2 - T_g^2} \left(\frac{H}{T}\right)^3 + \\ &+ \frac{a_5}{(T^2 - T_g^2)^3} \left(\frac{H}{T}\right)^5 + \dots \quad (5) \end{aligned}$$

where the values of the coefficients $a_3, a_5, \dots$, depend on spin dimensionality [8]. According to relation (5) all the non-linear terms of the magnetization diverge at T_g whereas the linear term follows a Curie-Weiss law. At T_g all the terms involved in relation (5) become significant even for small values of H/T and a limited expansion of the mean field equations contains odd and even powers of the magnetic field :

$$T = T_g \quad M = \frac{H}{T_g} - \frac{H^2}{T_g^2} \left(\frac{1}{\sqrt{2}}\right) + b \left(\frac{H}{T_g}\right)^3 + \dots \quad (6)$$

Comparison between relations (5), (6) and (3) gives $\gamma = 1$ and $\delta = 2$ for the S-K model.

The experimental investigation of the spin glass critical behaviour has confirmed many features predicted by the theoretical analysis. In $\text{AgMn} : 10\%$, Monod and Bouchiat showed that the magnetization is not described by the same analytic expansion above and below T_g [9]. In the spin glasses CuMn and AlGd Barbara *et al.* attempted to represent their experimental data by the scaling function (4b) [10]. Omari *et al.* analysed the non-linear susceptibility of $\text{CuMn} : 1\%$ above T_g using a limited expansion of the scaling function (4a) :

$$\chi_s = a_2 \tau^{-\gamma} H^2 + a_4 \tau^{-(2\gamma+\beta)} H^4 + \dots \quad (7)$$

and directly determined the values of the critical exponents γ and β [11]. They also fitted all the experimental data to the scaling function (4a). There are only few results concerning insulating spin glasses up to now. In the case of the amorphous manganese aluminosilicate Beauvillain *et al.* performed very careful measurements at $T > T_g$ and low values of the applied magnetic field. They analysed their data in the same way as Omari *et al.* and found an excellent fit to the scaling function (4a) ($T > T_g$). The value of the critical exponent β was found to be significantly greater than [12].

Postulating the absence of a thermodynamic transition at T_g , as suggested by theoretical spin glass models with short-range interactions and $d = 3$, [13] K. Binder argued that the commonly observed behaviour of χ_s above T_g could also be consistent with a zero degree transition. In this case the corresponding scaling function would read [14] :

$$\chi(H, T) = \frac{C}{T} \{ 1 - H^2 T^{-2-\gamma} C(HT^{-d}) \} \quad (8)$$

This scaling function implies that for sufficiently high values of the term HT^{-d} the static susceptibility deviates from the high temperature Curie-Weiss law. In this case a « plateau » or even a maximum of the susceptibility may be observed. From (8) T_g appears then as the temperature below which saturation of $\chi(H, T)$ occurs due to the existence of a finite field H .

In this paper we present an experimental study of the equilibrium magnetization of an insulating spin glass above and below T_g . We analyse the observed behaviour with both scaling functions (4a) (finite transition temperature) and (8) ($T = 0$ transition).

CsNiFeF_6 is a non-dilute random frustrated insulator. The magnetic ions (Ni^{2+} and Fe^{3+}) are randomly distributed on a network of cornersharing tetrahedra (site 16c of the space group $\text{Fd}\bar{3}\text{m}$). The magnetic interactions arise mainly from antiferromagnetic superexchange [15] between first neighbours [16]. The existence of antiferromagnetic interactions on a network where the elementary loops involve an odd number of spins is the source of magnetic frus-

tration. The absolute value of the Curie-Weiss temperature of CsNiFeF₆ ($\theta = -210$ K) [17] is very large compared to the temperature, where the Mössbauer spectra reveal the existence of a spontaneous local magnetization (6.1 K) [18] and this difference reflects the high degree of frustration of the compound.

From previous d.c. magnetization measurements we have determined a H - T spin glass like diagram [19]. These results showed the existence of a non-negligible positive J_0 compared to J : $J_0/J \cong 0.7$, and led to the determination of two characteristic temperatures at (extrapolated) zero field :

a) $T_M(0) = 4.75 \pm 0.05$ K, defined as the temperature of the maximum of the field cooled magnetization. The line $T_M(H)$ fits the de Almeida-Thouless line.

b) $T_R(0) = 5.35 \pm 0.05$ K, which corresponds to the temperature where the irreversibilities first appear. The line $T_R(H)$ approaches the T axis with a zero slope.

These two temperatures are distinctly separated and are both « candidates » for T_g . Therefore, the analysis of the non-linear susceptibility of CsNiFeF₆ was performed in order to determine the spin glass transition temperature and check the validity of a scaling hypothesis for this compound.

2. Experimental.

The magnetization measurements were performed by the extraction method on the same powdered sample as for the determination of the H - T phase diagram [14]. We also used the same apparatus and improved its resolution by amplifying the signal of the detection coils with a very reliable galvanometric amplifier (gain 10^3 - 10^4). The signal was then measured and amplified as previously [19].

For $T \geq 5.4$ K, the values of $M(H, T)$ correspond to first magnetization curves and were determined at constant T and increasing field ($0 \text{ G} \leq H \leq 100 \text{ G}$). Below 5.4 K, magnetic irreversibilities appear and this procedure no longer gives the equilibrium magnetization. In this region of temperatures the values of $M(H, T)$ correspond to the field cooled (f.c.) magnetization and were obtained by cooling the sample in the field of the measurement from 6 K down to T . In contrast to earlier very low field measurements [20] no dependence on the cooling rate has been detected with the fields used in these experiments.

The external field was produced by a multifilamentary superconducting coil. This device shows small hysteresis which is negligible for the magnetic fields used in this series of measurements ($0 \text{ G} \leq H \leq 100 \text{ G}$). The values of the field were corrected for the z -component of the residual field (H_{res}) due to the earth field and the metallic surroundings of the cryostat. The values of H_{res} were evaluated by linear regression of the variation of the magnetization with

the field, for the low values of H ($0 \text{ G} \leq H \leq 2 \text{ G}$), and were found to lie in between 0.6 G and 0.7 G.

The apparent susceptibility (M/H) takes very high values in the vicinity of $T_M(0)$ especially at the low fields, in agreement with our previous results [20]. Therefore, for the analysis of the data we had to take into account the demagnetizing field contribution ($H_{\text{dem}} = 4\pi DM$). In the case of a powdered sample the demagnetizing field is inhomogeneous and can only be roughly estimated. We determined D from the maximum value of the zero field cooled (z.f.c.) susceptibility of the isomorphous compound CsMnFeF₆, as obtained for the same sample holder and the same conditions of preparation of the sample⁽¹⁾. The values of H used in this paper have been determined as follows :

$$H = H_{\text{external}} - H_{\text{res}} - 1.66 M \quad (9)$$

(H in gauss and M in emu/cm³).

3. Results.

The values of $M(H)$ increase continuously when the temperature decreases from 5.99 K down to 4.8 K (Fig. 1). For $T \leq 4.8$ K, the magnetization decreases with temperature and the corresponding curves are not represented in figure 1.

By plotting M/H versus H^2 and extrapolating the observed behaviour at $H = 0$, we determined the initial f.c. susceptibility $\chi_0 = (M/H)_{H \rightarrow 0}$. The values of χ_0 have been further verified by performing a polynomial regression on the M/H versus H^2 data for $T \geq 5.6$ K and $0 \leq H \leq 20$ G.

χ_0 presents a well marked maximum at 4.77 K (Fig. 2). This temperature lies inside the error bars given for $T_M(0)$ [19]. At the maximum the value of χ_0

Fig. 1. — Set of magnetization curves between 4.8 K and 5.92 K.

⁽¹⁾ CsMnFeF₆ has a small spontaneous moment and its susceptibility measured in very small applied fields reaches the value of the inverse of the demagnetizing factor.

Fig. 2. — Linear susceptibility χ_0 versus temperature. χ_0 is defined as : $\chi_0 = \lim_{H \rightarrow 0} \frac{M}{H}$.

is equal to 0.4 emu/cm³. Without the correction for the demagnetizing field we obtain $\chi_0 = 0.24$ emu/cm³, in agreement with the value determined at $H = 30$ mG [20].

For $5.4 \text{ K} \leq T \leq 6 \text{ K}$, the linear variation of $1/\chi_0$ with T (Fig. 3) leads to the determination of an effective Curie-Weiss law :

$$\chi_0 = \frac{C}{T - \theta} \text{ with } C = 0.705 \text{ emu/mole and } \theta = 5.23 \text{ K.} \quad (10)$$

The values of the molar Curie constant and of the Curie-Weiss temperature are slightly different from those determined in a larger temperature range going

Fig. 3. — Inverse linear susceptibility as a function of the temperature. The full straight line shows the fitted Curie-Weiss law above 5.37 K.

from $\sim 6 \text{ K}$ up to 15 K [19]. This difference indicates that the effective Curie-Weiss law is an approximation valid in the narrow temperature range involved. We note that the value of the molar Curie constant of the high temperature ($T \gtrsim 150 \text{ K}$) Curie-Weiss law is equal to 5.63 emu/mole.

4. Analysis for a finite T_g .

4.1 QUALITATIVE ANALYSIS — DETERMINATION OF T_g . — The non-negligible positive value of θ derived from the effective Curie-Weiss law and the strong dependence of χ_0 on T (χ_0 varies by two orders of magnitude between 5.99 K and 4.8 K) indicate that CsNiFeF_6 , in spite of the strong n.n. antiferromagnetic interactions, behaves in the vicinity of T_g almost as a ferromagnet. The comparison between the line $T_M(H)$ and the de Almeida-Thouless line [7], has already led to a non-negligible positive mean value of the ratio J_0/J [19]. Therefore our data cannot be analysed within the approximation $J_0/J = 0$.

In the absence of a spin-glass critical behaviour, the temperature dependence of χ_s is directly related to that of $\chi_0(T)$. In this case, an adequate normalization of the magnetic field with respect to $\chi_0(T)$, leads to a universal curve for $\chi_s(H, T)$. This normalization is necessary in the investigation of a spin glass critical behaviour, especially in our case, where χ_0 becomes important and varies rapidly with temperature in the vicinity of T_g .

Omari *et al.* analysed the data of $\text{CuMn} : 1\%$ above T_g , according to the following expansion of the magnetization in terms of odd powers of the normalized field H^* :

$$M = H^* - a_3 H^{*3} + a_5 H^{*5} + \dots \quad (11)$$

$$\text{with } H^* = \chi_0 H = \frac{C}{T - \theta} H.$$

This normalization of the magnetic field accounts for a non-zero θ/T_g independent of the value of the ratio J_0/J . The authors argued that in their system J_0/J is zero and θ has a quantum mechanical origin.

A positive θ/T_g related to J_0/J implies a ferromagnetic component (J_0) superimposed to disorder (J). In the absence of disorder ($J = 0$), J_0 should lead to a ferromagnetic phase and an associated Curie temperature (T_c). If this hypothetical T_c is significantly lower than T_g , it seems reasonable to make a mean field approximation for the ferromagnetic component and replace H by $H + J_0 M$ in relations (4), (5), (6) and (7). The Sherrington-Kirkpatrick solutions (5) and (6) extended to $J_0 \neq 0$ are then :

$$T > T_g : \quad M = \frac{H}{T - J_0} - \frac{a_3}{T^2 - T_g^2} \left(\frac{H}{T - J_0} \right)^3 \frac{T}{T - J_0} + \frac{a_5}{(T^2 - T_g^2)^3} \left(\frac{H}{T - J_0} \right)^5 \frac{T}{T - J_0} + \frac{a'_5}{(T^2 - T_g^2)^2} \left(\frac{H}{T - J_0} \right)^5 \frac{TJ_0}{(T - J_0)^2} + \dots \quad (12)$$

$$T = T_g : M = \frac{H}{T_g - J_0} - \frac{1}{\sqrt{2}} \frac{H^2}{(T_g - J_0)^3} + \frac{H^3}{(T_g - J_0)^5} \{ b - J_0(1 - b) \} + \dots \quad (b)$$

For $T \gtrsim T_g$ the last term of (12a) becomes negligible compared to the third term. A more general form of the magnetization above T_g is obtained from relation (7) :

$$T > T_g : M = \frac{H}{T - J_0} - \frac{a_3}{\tau^\gamma} \left(\frac{H}{T - J_0} \right)^3 \frac{T}{T - J_0} + \frac{a_5}{\tau^{2\gamma+\beta}} \left(\frac{H}{T - J_0} \right)^5 \frac{T}{T - J_0} + \frac{a_{5'}}{\tau^{2\gamma}} \left(\frac{H}{T - J_0} \right)^5 \frac{TJ_0}{(T - J_0)^2} + \dots \quad (13)$$

(13) has been written in such a way as to find the mean field relation (12a) by setting $\gamma = 1$ and $\beta = 1$.

Figures 4 and 5 represent $M/\chi_0 H$ versus $(\chi_0 H)^2$ and $\chi_0^3 H^2 T$ respectively. The plot of figure 4 comes from relation (11), and that of figure 5 accounts for the influence of χ_0 on the first term of χ_s as suggested by relation (13). Both figures lead to the same qualitative result : for $T \gtrsim 5.33$ K, the non-linear susceptibility has a very strong temperature dependence whereas, at $T \lesssim 5.33$ K, the values of $M/\chi_0 H$ are almost independent of T , at least for low values of the abscissa. In both figures there is no particular variation of χ_s close to the temperature of the maximum of χ_0 ($T_M(0) = 4.75 \pm 0.05$ K). As far as the observed behaviour of the non-linear susceptibility provides a criterion for the determination of T_g , in CsNiFeF₆ this temperature must lie between 5.38 K and 5.33 K and thus associated to $T_{R1}(0)$, i.e. the temperature where magnetic irreversibilities first appear.

As already noted, in a spin glass all the non-linear terms of the magnetization are expected to diverge at $T_g(0)$. Consequently, the closer T approaches T_g from above, the more terms are needed for adjusting $M(H)$ in a given window of H , if the expansion in odd powers of the magnetic field is used. A computer performed linear regression on our data showed that at $T = 5.84$ K the magnetization between 0 G and 60 G could be fitted with only three terms, whereas at 5.43 K and in a more reduced field range ($0 \leq H \leq 10$ G) 10 terms were needed to obtain the same quality of the fit. This result confirms that $T_{R1}(0)$ is a peculiar temperature for the non-linear susceptibility of CsNiFeF₆ and further supports the previous idea of associating it to the spin glass transition temperature.

4.2 QUANTITATIVE ANALYSIS. — In the following analysis we will assume that the large value of θ is essentially equivalent to a large ferromagnetic mean value J_0 of the interactions. This leads to $J_0/J = \theta/T_g = 0.98$ (J being the width of the distribution of interactions). The value of 0.98 is larger, but remains coherent with the result ($J_0/J = 0.7$) derived from the analysis of the H - T phase diagram [19].

4.2.1 Determination of the critical exponent γ . — According to relation (13), the critical exponent γ can be determined from the divergence (if any) of the

Fig. 4. — $M/\chi_0 H$ as a function of $(\chi_0 H)^2$ for different temperatures.

Fig. 5. — $M/\chi_0 H$ as a function of $\chi_0^3 H^2 T$ for different temperatures.

coefficient A_3 defined from the following expansion of χ_s :

$$T > T_g \quad \chi_s = A_3 H^2 + A_5 H^4 + A_7 H^6 + \dots \quad (14)$$

The correct evaluation of A_3 is difficult in the vicinity of T_g since all the coefficients in (14) diverge at T_g . Therefore, as T approaches T_g , the analysis

of χ_s must be restricted to lower fields. In CsNiFeF_6 , the high value of J_0 amplifies this effect. According to relation (13), at $\tau = 0.01$, the ratio A_3/A_5 is almost by two orders of magnitude smaller for $J_0/J = 0.9$ than for $J_0/J = 0$.

At low fields experimental errors are important, and the determination of A_3 becomes much less accurate in the vicinity of T_g . Figure 6 shows some values of A_3 , as determined for $T \geq 5.43$ K, versus the reduced temperature τ , on a log-log scale. We considered that T_g is equal to $T_{R1}(0) : T_g = 5.35$ K. The error bars correspond to the estimated error on the determination of the initial slope of M/H versus H^2 . They do not include the additional contribution due to the influence of higher order terms than A_3 on the estimated value of the initial slope. This contribution increases as T approaches T_g , and is the origin of the observed deviation from the ideal power law expected for A_3 (see [32]).

As seen in figure 6, the term A_3 increases by two orders of magnitude between 5.99 K and 5.43 K. A mean value of $\gamma = 2.5$ can be deduced. However the most probable value is $\gamma = 3$ which best fits the data for $\tau > 5 \times 10^{-2}$. We note that, in the same temperature range, χ_0 varies only by a factor of 4.

4.2.2 Determination of the critical exponent β . — The reported experimental determinations of the exponent β have mostly been done in the paramagnetic region, from the divergence of the coefficient A_5 in relation (14) [11, 12]. Due to the large value of χ_0 in CsNiFeF_6 , which already makes it difficult to separate A_3 from the other coefficients of the expansion, it is impossible to derive A_5 . In the ordered phase, β is defined by the temperature dependence of the order parameter at zero field :

$$T \leq T_g \quad q \sim \tau^\beta. \quad (15)$$

Fig. 6. — Coefficient A_3 as a function of τ in log-log scale.

According to the Parisi scheme of replica-symmetry breaking [21], the spin glass order parameter is a continuous and monotonic function $q(x)$, defined between 0 and 1. The value $q(1)$ is equal to the Edwards-Anderson order parameter. In this replica symmetry breaking scheme, the susceptibility is related to the order parameter by the formula

$$(H \rightarrow 0) \quad \frac{M}{H} = \frac{C}{T}(1 - q), \quad q = \int_0^1 q(x) dx \quad (16)$$

C/T is the paramagnetic linear susceptibility ($J_0 = 0$). At $T \geq T_g$, the function $q(x)$ is a delta function centred at $x = 1$ leading to $q = q_{E.A.}$. Below T_g , $q(x)$ evolves continuously with temperature and q differs from $q_{E.A.}$ as the temperature decreases below T_g .

The critical exponent β is derived from the zero field temperature dependence of q :

$$T \lesssim T_g, \quad H = 0, \quad q = a\tau^\beta = \frac{T}{C} \left(\frac{C}{T} - \lim_{H \rightarrow 0} \frac{M}{H} \right) \quad (\text{case } J_0 = 0). \quad (17)$$

At a given temperature $q(H = 0)$ is proportional to the difference between the extrapolated Curie-Weiss law and the linear susceptibility. Thus T_g corresponds to the temperature below which the linear susceptibility deviates from the paramagnetic law. This agrees with our experimental results. As seen in figure 3, in CsNiFeF_6 χ_0 follows an apparent Curie-Weiss law down to a temperature ($T = 5.37$ K) comparable to the value of T_g previously determined from the behaviour of the non-linear susceptibility.

Relation (17) had been derived for the case $J_0 = 0$. In order to extend it to the case $J_0 \neq 0$, the applied field H has to be changed into the mean local field $H_1 = H + J_0 M$. The initial susceptibility with respect to the local field $\lim_{H_1 \rightarrow 0} \frac{M}{H_1} = \chi_0^1$ is obtained from the susceptibility χ_0 by the relation :

$$\chi_0^1 = \frac{\chi_0}{1 + J_0 \chi_0} \quad (18)$$

$\chi_0^1(T)$ is represented in figure 7. Above T_g , χ_0^1 follows a Curie law with the same Curie constant as χ_0 . Below T_g , χ_0^1 varies slowly with temperature and has only a very smooth maximum at $T_M(0)$. It looks very similar to the field cooled susceptibility of classical spin glasses with $J_0 = 0$.

The temperature dependence of $q(H = 0)$ is represented in figure 8. The observed behaviour leads to $1.1 \lesssim \beta \lesssim 1.3$ and $T_g = 5.37$ K. It must be noticed that, due to the very large range of temperature in which the power law τ^β is valid, the value of β does not depend much on the exact value of T_g (whether 5.35 or 5.37).

A similar approach for the evaluation of β has already been used in other papers [31], but the order

Fig. 7. — Linear susceptibility χ_0^1 with respect to the mean local field *versus* temperature. χ_0^1 is defined as $\chi_0^1 = \lim_{H+J_0M \rightarrow 0} \frac{M}{H+J_0M}$. The full line corresponds to the Curie law.

Fig. 8. — $q = T\left(\frac{C}{T} - \chi_0^1\right)$ as a function of temperature. The full lines correspond to a τ^β behaviour $\beta = 1.1, 1.2, 1.3$.

parameter considered in these papers was taken as $q_{E.A.}$.

4.2.3 Fit of the data on a scaling function. — The analysis of the critical behaviour at $T > T_g$ has been made on the basis of relation (13). If this relation is expressed in terms of the mean local field $H_1 = H + J_0 M$ rather than in terms of the applied field H , it gets the form of an expansion of a scaling function written as :

$$\chi_s = \tau^{+\beta} F\left(\frac{H_1^2}{T^2} \frac{1}{\tau^{\beta+\gamma}}\right) \quad (19)$$

$$\text{with } \tau = \frac{T - T_g}{T}.$$

This is a generalized form of relation (4a) suggested by Omari *et al.* [11]. It has been checked using the previously derived values for T_g , β and γ . The result is shown on figure 9 with $T_g = 5.37$ K, $\beta = 1.2$ and $\gamma = 3$.

The values of χ_s were determined above and below T_g from the relation :

$$\chi_s = T\left(\frac{C}{T} - \frac{M}{H + J_0 M}\right) \quad (20)$$

with $C = 8.4 \times 10^{-3}$ emu/cm³ ($= 0.705$ emu/mole) and $J_0 = \theta/C$ ($\theta = 5.23$ K). The function $F(x)$ tends toward a non-zero value as $x = H_1^2/(T^2 \tau^{\beta+\gamma})$ goes to zero for $T < T_g$. This reflects the finite values of the order parameter for $H = 0$ in this range of temperature. The straight lines in figure 9 indicate the

Fig. 9. — Scaling function : plot of $\log \{ \chi_s / \tau^\beta \}$ *versus* $\log \{ h^2 / \tau^{\beta+\gamma} \}$ where $h = (H + J_0 M)/T$. The values of the parameters are $T_g = 5.37$ K, $\beta = 1.2$, $\gamma = 3$. The straight lines represent the asymptotic behaviours : $\chi_s \propto h^2 / \tau^\gamma$ ($T > T_g$, small h), $\chi_s \propto h^{2/\delta}$ ($\tau \rightarrow 0$).

Fig. 10. — Detail of the scaling function ($|\tau| < 0.05$).

asymptotic behaviour of F for $x \rightarrow 0$ ($T > T_g$) and $x \rightarrow \infty$ ($T \rightarrow T_g$):

In the limit $x \rightarrow 0$ ($T > T_g$), $F(x)$ varies as x . This behaviour is in agreement with relation (3a).

In the limit $x \rightarrow \infty$ ($T \rightarrow T_g$), $F(x)$ varies as $x^{\beta/(\beta+\gamma)}$. This agrees with relation (3b) if the exponent δ is related to β and γ by $\beta(\delta - 1) = \gamma$, which is indeed one of the classical scaling relations ($\delta = 3.45$).

In figure 9, the scaling function has been plotted in the range $|\tau| \lesssim 0.1$ and $H < 100$ G. The fit is quite good especially in the vicinity of T_g as can be seen in figure 10 where the temperature range has been limited to $|\tau| \lesssim 0.05$. In this range the magnetization curves at different temperatures are seen to be an exact continuation of each other. In the paramagnetic region, for larger values of τ the scattering of data becomes important since this is the region of small fields and thus of larger errors.

Attempts to build up a universal function with different values of T_g , β and γ have been made. Due to the definition of q , T_g is set by the choice of the Curie-Weiss law which fits the data of χ_0 above $T_g(q(H=0))$ becomes non-zero as soon as χ_0 deviates from the Curie-Weiss law). The temperature range of the fit for this law is $T < 6$ K. The error bars on the parameter C and θ lead to $T_g = 5.37 \pm 0.2$. Within this range of T_g , the values of β and γ are determined by the possibility of defining a continuous scaling function. They are found to lie within the same limits as previously estimated:

$$\beta = 1.2 \pm 0.1 \quad \gamma = 3 \pm 0.5. \quad (21)$$

4.3 RELATION TO THE SPECIFIC HEAT AND THE H - T PHASE DIAGRAM. — From the values of β and γ and using relation:

$$\alpha + 2\beta + \gamma = 2 \quad (22)$$

we deduce $\alpha = -3.4 \pm 0.5$. This highly negative value of the exponent related to the specific heat explains the absence of divergence of the magnetic specific heat at T_g [22]. A divergence should only be observed on the third derivative of the specific heat with respect to the temperature. We note that the curve $C^m(T)$ (Fig. 2 of [22]) presents an abrupt change of slope at the spin glass critical temperature (in [22] T_g was determined from the maximum of χ_0 and not from the appearance of the magnetic irreversibilities).

The change of slope of $C^m(T)$ at T_g leads to a net maximum of the temperature derivative of the magnetic entropy at T_g . This is seen in a C^m/T versus T plot (Fig. 11) obtained from our previous data. The maximum of C^m/T is more pronounced than in other

Fig. 11. — C^m/T versus temperature. C^m is the magnetic specific heat.

spin glasses [23] and this may be due to the absence of magnetic dilution in our compound : the contributions arising from spins which do not belong to the infinite magnetic cluster are smaller than in dilute systems.

In a recent communication S. E. Barnes *et al.* [24] showed that the temperature and field dependence of the transverse freezing line in spin glasses is closely related to the critical exponent δ :

$$\tau \sim h^{4/\delta} . \quad (23)$$

This line coincides with the Gabay-Toulouse line [25] for the mean-field value $\delta = 2$. In reference [19] we compared the line $T_{R1}(h)$ where the irreversibilities first appear in the d.c. magnetization curves of CsNiFeF₆ with the Gabay-Toulouse line. Figure 12 represents the experimental points of $T_{R1}(h)$ as compared to transverse freezing lines given by (23) with $\delta = 2$ and $\delta = 3.45$.

5. Analysis for $T_g = 0$.

According to relation (8), in the case of $T_g = 0$, the divergence of the first term of the non-linear susceptibility (A_3) with respect to the temperature gives the critical exponent Γ . We used the values of A_3 determined above 5.35 K, i.e. the temperature range where we were able to detect an H^2 term in χ_s at low fields. As seen in figure 13, $\log(A_3)$ has a linear variation with $\log(T)$, but the resulting values for Γ are very large, lying between 70 and 80.

If the transition occurs at $T = 0$, then the disorder is assumed to be high enough so that a positive J_0 cannot give rise to a Curie temperature. However, according to reference [14], J_0 can induce a well defined maximum in the very low field susceptibility. This consideration agrees with the behaviour of CsNiFeF₆. In order to test the validity of the scaling function (8),

Fig. 12. — Experimental points of the $T_{R1}(h)$ line. $T_{R1}(h)$ is the temperature at which irreversibilities first appear on the d.c. magnetization at a given reduced field h ($h = g\mu_B H/kT_g$). The full lines correspond to transverse freezing lines given by $\tau \sim h^{4/\delta}$ with $\delta = 2$ and $\delta = 3.45$.

Fig. 13. — Coefficient A_3 versus temperature in log-log scale.

Fig. 14. — Plot of $\log \left\{ \left(C - \frac{M}{h} \right) \frac{T^\Gamma}{h^2} \right\}$ versus $\log \left(\frac{h}{T^\Delta} \right)$ where $h = (H + J_0 M)/T$ ($\Gamma = 80$, $\Delta = 45$).

we used the mean value of the local fields rather than the applied field, as in the previous section. In the region where the magnetization is reversible ($T > 5.37$ K), we could define a universal function for a very high value of the critical exponent Δ ($\Delta = 45 \pm 5$). However, the data of χ_s below 5.37 K could not be well fitted to this universal function. Figures 14 and 15 show indeed that, while the data corresponding to $T > 5.37$ K are correctly scaled, the data corresponding to $T < 5.37$ K do not lie on a single curve. Figure 15 presents the results for $T < 5.37$ K in more detail, the magnetization curves at different temperatures are seen to be parallel to each other and do not define a continuous function.

Fig. 15. — Detail of the plot of $\log \left\{ \left(C - \frac{M}{h} \right) \frac{T^\Gamma}{h^2} \right\}$ versus $\log \left(\frac{h}{T^\Delta} \right)$ for $T < 5.37$ K.

The unphysical high values of the exponents Γ and Δ may suggest that, for this compound, the divergence of the correlation length, as T approaches $T_g = 0$, is exponential, of the type $\exp(\text{const.}/T)$. Such a divergence is expected if the system is right at its lower critical dimensionality. However it is difficult to distinguish an exponential divergence from a power law if the temperature is not close enough to the transition temperature. For CsNiFeF_6 , plotting $\log \left\{ \left(C - M/h \right) \exp(\Gamma/T)/h^2 \right\}$ versus $\log \left\{ h/\exp(\Delta/T) \right\}$ leads to the same qualitative result as that shown in figures 14 and 15. In this case the values of the critical quantities Γ and Δ have been found to be equal to 400 and 300 K respectively. Arguing on these values is not as straightforward as for critical exponents. However, we note that they are extremely high compared to the temperature where the divergence of the correlation length is assumed to affect the thermodynamic properties of the system.

Our results indicate that the scaling for $T_g = 0$ fails in describing the deviations of the equilibrium magnetization from the paramagnetic behaviour below 5.37 K. Scaling relation (8) postulates that the linear susceptibility remains in the Curie-Weiss form down to 0 K. Our experimental values for χ_0 which correspond to the linear susceptibility show that the deviations from the paramagnetic behaviour below 5.37 K affect both the linear and the non-linear susceptibility and that they are not simply induced by the finite value of the applied field. This is also indicated by the monotonic decrease of the temperature of the maximum of the field cooled magnetization when the applied field increases [19]. The validity of the scaling

function (8) implies that, at least for low values of the applied field, this temperature should increase with the field.

It may be argued that the deviations of χ_0 from the paramagnetic behaviour are due to the finite time scale of our experiment. However this assumption does not explain the large unphysical values of the exponents Γ and Δ .

6. Conclusion.

The analysis of the equilibrium magnetization of CsNiFeF_6 strongly supports the assumption of a well defined spin glass transition temperature at 5.37 K. The possibility of scaling the whole set of experimental data to a continuous universal function in both the *ordered* and the *paramagnetic* regions with the same values of the critical exponents is a significant result. It is in agreement with a general scaling argument which predicts symmetrical critical behaviour above and below the critical temperature.

Usually the fit of the scaling function is limited to the paramagnetic region. In order to extend it to the ordered region, the non-zero value of J_0 has to be taken into account. This was done by using the mean value of the local fields $H_l = H + J_0 M$ instead of the applied field as an appropriate variable. The scaled parameter χ_s has been defined above and below T_g by $\chi_s = T \left(\frac{C}{T} - \frac{M}{H_l} \right)$. Above T_g , χ_s is the usual non-linear susceptibility; below T_g , χ_s is proportional to $q = \int_0^1 q(x) dx$, i.e. the quantity related to the spin glass order parameter in the Parisi scheme of replica symmetry breaking [21].

Symmetrical critical behaviour below and above T_g has already been observed in the amorphous alloy GdAl [26] but our approach differs from that of Malozemoff and Imry in that we consider non-zero values of χ_s below T_g at zero field, which allows us to plot all the data on the same diagram. The symmetry of the critical behaviour has also been restored in the mean field theory for spin glasses in reference [27]. In this reference it has been pointed out that the projection hypothesis implying that, below T_g , q depends only on the temperature is not valid in the vicinity of T_g . The relations given for the susceptibility below T_g in [27] imply $\gamma = \gamma'$.

The values of the exponents β and γ in CsNiFeF_6 ($\beta = 1.2 \pm 0.1$, $\gamma = 3 \pm 0.5$) are very close to those of the amorphous manganese aluminosilicate [12] ($\beta = 1.4 \pm 0.1$, $\gamma = 3.1 \pm 0.1$). We note that in both insulating spin glasses β is found to be greater than 1. These values of β explain the absence of a maximum of the field cooled magnetization at T_g in both systems. As pointed out by H. Bouchiat [28], in the case of $\beta > 1$, a maximum in χ_0 should only appear below T_g .

From our analysis, all the results of static measurements (specific heat, magnetization) are consistent with the existence of a finite spin glass critical temperature for CsNiFeF₆. The high value of the ratio T_g/θ (~ -40) may indicate that the ordering phenomena observed in our compound are due to interactions of higher order than the main nearest neighbour anti-ferromagnetic interactions. If T_g gives an order of magnitude for these interactions then their value should be almost 40 times lower than that of the nearest neighbour interactions.

The possibility of observing a static behaviour in complete agreement with the existence of a true thermodynamic phase transition is related to the time scale of the measurements. In the case of classical ferromagnets, the experiments are made on samples with finite size hence with no true phase transition. The observation of properties related to a transition in these samples is only due to the fact that the used sizes are large enough to give very high characteristic relaxation times as compared to the time scale of the experiment. The same holds for spin glasses: the onset of a magnetic state whose characteristic relaxation times may be of order 10^{20} s [28] has all the properties of a phase transition.

We finally note that, very recently, a true thermodynamic phase transition at finite temperature has been observed by computer simulation in three-dimensional Ising models for large sizes of the samples [30]. This result further supports the validity of the experimental findings concerning the spin glass critical behaviour.

Note added in proof.

The results of the analysis reported in this paper strongly depend on the Curie-Weiss behaviour $C/(T - \theta)$ derived for the linear susceptibility χ_0 between 5.4 K and 6 K. The values of C and θ ($J_0 = \theta/C$) used in the determination of the scaling function condition the values derived for the freezing temperature T_g and the critical exponents γ and β .

As already mentioned in the text, the values of χ_0 have been verified between 5.6 K and 6 K by a polynomial regression of the M/H versus H^2 data for $0 < H < 10$ G. In this range of temperature and field, the expansion of M/H in terms of H^2 is justified owing to the value of T_g ($= 5.37$ K). This procedure has confirmed the proposed values of C and θ .

In the vicinity of T_g , the determination of χ_0 by a

Fig. 16. — Temperature dependence of the coefficient A and the exponent α , as derived from the fits of MT/H_1 to the power law $A - BH_1^\alpha$ at different given temperatures. H_1 is the mean local field $H + J_0 M$. A is equal to $\chi_0^1 T$ where χ_0^1 is the linear susceptibility with respect to H_1 .

linear extrapolation of M/H versus H^2 is not justified owing to the various values of H . The extrapolated values of χ_0 below 5.4 K have only been used for a first estimate of β which has been further checked in the determination of the scaling function.

Near T_g , M/H_1 , where H_1 stands for the mean local field $H + J_0 M$, should behave as $\chi_0^1 - BH_1^\alpha$. χ_0^1 is the linear susceptibility with respect to H_1 . The exponent α is expected to decrease from 2 down to $2/\delta$ ($\delta = 3.45$) between 6 K and the freezing temperature T_g , and the coefficient B should increase regularly in the same temperature range. The data of MT/H_1 have been fitted to power laws in H_1 at different given temperatures T . $H_1 = H + J_0 M$ was calculated with the value of J_0 used throughout our analysis. The results for $\chi_0^1 T$ and α are reported in figure 16 as a function of T . The values of the Curie constant C , the freezing temperature T_g , and the exponent δ derived in the paper are seen to be consistent with the present results.

Acknowledgments.

The authors are indebted to H. Bouchiat, N. Boccara, R. Bidaux, J. P. Carton, P. Monod and L. de Seze for many fruitful discussions and remarks. They also thank R. Gérard Deneuille and B. Bollendorf for their technical assistance.

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- [32] *Note added in proof.* — The plot of the scaling function in figure 9 shows that the non-linear susceptibility behaves as H^2/τ' only for values of x smaller than about 20. In figure 10, which shows a detail of the same scaling function, magnetization data obtained at a given temperature are represented by the same character. In this figure it can be seen for instance that the points corresponding to the smallest applied fields at 5.48 K (curve B) are located around $x = 25$ which is far outside the range of interest. The same is true for all magnetization curves obtained at $\tau < 5 \times 10^{-2}$. This means that the procedure of evaluation of A_3 strongly underestimates this coefficient below $\tau = 5 \times 10^{-2}$.