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Influence of the mechanical grinding on the magnetic properties of $GdMn_2$

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Abstract

The cubic C15 phase $GdMn_2$ was submitted to high-energy ball milling. The resulting products were investigated by X-ray powder diffraction, scanning electron microscopy, ac-magnetic susceptibility and dc-magnetization measurements. With increasing speed of the milling treatment, amorphization of the sample appears, as shown by X-ray diffraction analysis. Furthermore, this treatment induces a magnetic transition from antiferromagnetism (unmilled sample) to ferromagnetism below $T_C \cong 105(5)$ K (milled sample at high speed). This effect is compared with that of the application of hydrostatic pressure on $GdMn_2$.

Keywords: Rare earth compounds; Transition metal compounds; Amorphous alloys; Powder metallurgy; Magnetic measurements

1. Introduction

$GdMn_2$ which crystallizes in the cubic C15 Laves phase (*Fd3m* space group, $MgCu_2$-type structure), presents interesting magnetic behaviour: (i) a recent investigation using elastic neutron scattering measurements performed on powder and single-crystal samples confirms that this intermetallic orders antiferromagnetically below $T_N = 105$ K [1]. The magnetic moments relative to Mn (2.1(1) μ_B) and Gd (4.6(1) μ_B) form a non-collinear arrangement of a geometrically frustrated antiferromagnet; (ii) a second magnetic transition appears below $T_1 = 35$ K with the occurrence of a spontaneous magnetization [2,3]. This low temperature magnetic ground state denoted ferromagnetic was detected only by magnetization and electrical resistivity measurements.

It is well known that the antiferromagnetic order of the Mn-atoms in the compounds $REMn_2$ (RE=rare earth) is governed by the Mn–Mn interatomic distances (d_{Mn-Mn}) [4]. Above a critical value of $d_{Mn-Mn} \cong 0.266$ nm, the Mn-atoms have a large magnetic moment. On the contrary, for the intermetallics $REMn_2$ formed with the smallest rare earths such as Ho or Er, the Mn-atoms do not bear a magnetic moment and the compounds exhibit ferromagnetic ordering attributed to the RE moments only. Under these conditions, the magnetic properties of the $REMn_2$ Laves phases are strongly sensitive to an applied hydrostatic pressure as already shown for $GdMn_2$ [5,6]: (i) above a critical pressure of 14.8 kbar, the Mn sublattice magnetic moment disappears since the d_{Mn-Mn} interatomic distances are smaller than 0.266 nm; (ii) its Néel temperature T_N decreases strongly -5.9 K/kbar with increasing pressure; (iii) for pressure higher than 12 kbar only ferromagnetic ordering ($T_C \cong 110$ K) is detected. In this case only the Gd–Gd magnetic interaction of the Ruderman–Kittel–Kasuya–Yosida (RKKY) type occurs.

Mechanical milling was used to modify the crystallographic and magnetic properties of several Laves phase compounds such as $GdAl_2$ [7], $GdCo_2$ and $GdFe_2$ [8] and GdX_2 with X=Pt, Ir, Rh, Al and Mg [9]. This process, applied for instance on the cubic intermetallic $GdPt_2$, induces with increasing milling time both a decrease of the unit cell parameter and an increase of the Curie temperature [9]. This behaviour was explained on the basis of the RKKY interaction. The reinforcement of the ferromagnetic Gd–Gd coupling is correlated to a decrease of the d_{Gd-Gd} interatomic distances. In this view, it is interesting to undertake mechanical grinding on $GdMn_2$. We report here, the effect of this mechanical treatment on both the structural and the magnetic properties. This effect is compared with that using the hydrostatic pressure.

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2. Experimental details

A polycrystalline sample of $GdMn_2$ was synthesized by arc melting of the pure elements (3N for Gd and Mn) in stoichiometric ratio and in a purified argon gas atmosphere. The alloy button was turned upside down and remelted 4 times in order to ensure complete homogenization. Afterwards, the ingot was annealed under vacuum at 1073 K for 2 weeks. Then, the sample was pulverized and sieved at 100 μm.

Mechanical grinding was performed using a Fritsch pulverisette five-planetary mill. The device consists of a hardened-steel cylindrical container with an inner diameter of 4 cm and a volume of 80 cm^3. The milling tool used consisted of six steel balls (diameter=10 mm; weight≅4 g). In order to prevent reaction with oxygen or nitrogen, 1.6 g of the screened $GdMn_2$ sample was sealed, with an atmosphere (P=0.1 MPa) of purified argon gas, in a hermetic way in the hardened-steel container. The ball-to-powder weight ratio was maintained at ≅15. The powder was ground for 12 h at various rotation speeds of the plateau (i.e. from 200 to 300 rpm).

The samples were characterized before and after mechanical grinding by X-ray powder diffraction (Philips diffractometer using Cu Kα radiation). The morphology and size of the particles produced by mechanical grinding were examined using a Jeol 840 microscope. The particle size distribution was determined using a Laser Scattering Particle Size Analyser (Malvern 2000S apparatus, range from 20 to 2 mm). For this analysis, the sample was immersed in ethanol.

The magnetization of the initial and ground samples were measured between 4.2 and 300 K in applied fields up to 4 T using a SQUID magnetometer.

3. Results and discussion

Fig. 1 shows the X-ray powder patterns of the initial $GdMn_2$ sample before and after mechanical grinding for 12 h at various rotation speeds. The pattern of the unmilled sample is easily indexed on the basis of the cubic $MgCu_2$-type structure. The unit cell parameter a=0.776(1) nm is consistent with that given in the literature [5]. After grinding, drastic changes are observed. The peaks in the pattern of the ground sample at 200 rpm are considerably broadened and already a large number of them have totally disappeared. The broadening of the peaks is due to the reduction of the crystallite size (≅12(2) nm for this last sample). After grinding at 300 rpm, X-ray diffraction lines no are not observed and only a very broad and diffuse diffraction line centered around $2\theta \cong 35°$ characteristic of amorphous material occurs.

Representative SEM images for the particles ground under two different rotation speeds are shown in Fig. 2. It is clearly visible that the particles obtained at 200 rpm have a larger size distribution: (i) some of them are

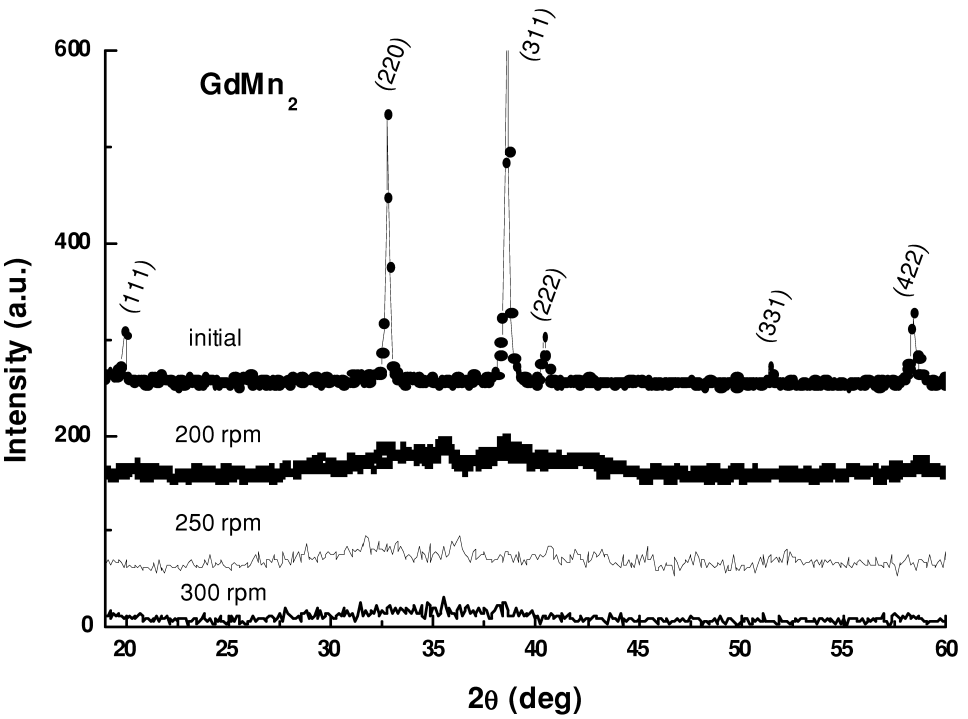

Fig. 1. X-ray powder pattern of $GdMn_2$ before (initial) and after mechanical grinding for 12 h at various rotation speeds.

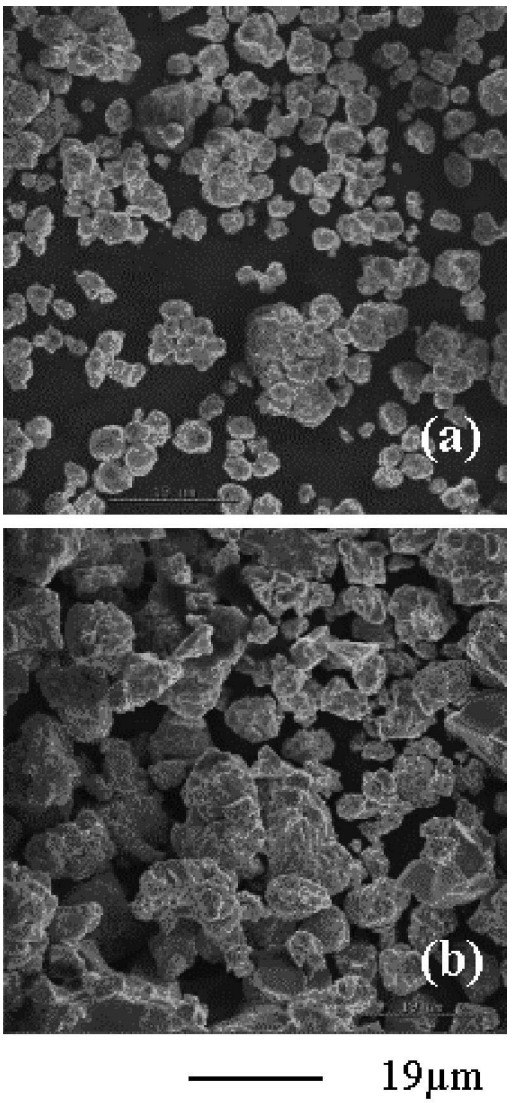

Fig. 2. SEM micrographs of the $GdMn_2$ particles obtained by mechanical grinding for 12 h at rotation speed 200 (a) and 300 rpm (b).

isolated and spherical ($\cong$2–4 μm in diameter); (ii) but many form aggregates. The size distribution is more reduced after grinding at 300 rpm but this process induces an enlargement of the particles. In other words, the increase of the rotation speed favours the formation of bigger aggregates. This reflects the dominating effect of the cold-welding at high speed.

In order to obtain more information, the particle size distribution of each sample has been measured (Fig. 3). The initial sample has a large and inhomogeneous distribution showing a maximum around 23 μm. After grinding at 200 rpm, the distribution is still large but the maximum shifts towards low diameter around 13 μm. The formation of aggregates in this last sample is clearly highlighted as a shoulder appears near 91 μm. The grinding at 200 rpm induces a decrease of the average diameter (23→13 μm) of the $GdMn_2$ particles but involves also the occurrence of aggregates. On the contrary, a much more homogeneous particle size distribution appears for samples obtained by grinding at higher rotation speed such as 300 rpm. However the average diameter increases with increasing the rotation speed and reaches 25 μm for the higher value (300 rpm). These observations agree with those deduced from the SEM examination.

The temperature dependences of the magnetization (M) of the unmilled and ground $GdMn_2$ samples, measured in a low field $\mu_0 H = 0.05$ T, are given in Fig. 4. We measured M with a monotonically decreasing temperature in an applied magnetic field (FC, field cooled process). The $M = f(T)$ curve of the initial $GdMn_2$ sample exhibits two distinct features: (i) around 110(1) K a small but abrupt increase of the magnetization is observed (see inset in Fig. 4) (this temperature is in good agreement with the Néel temperature values $T_N = 105$ or 108 K found in the literature [1,2]); (ii) with decreasing temperature, M increases strongly near $T_1 = 40(1)$ K (temperature defined by a minimum in the derivative curve $\delta M/\delta T = f(T)$) and then tends to saturate at lower temperature. This behaviour characterizes the second magnetic transition detected previously for instance at 35–40 K by thermal expansion measurements [10].

The magnetic transition observed at T_N is very sensitive to the mechanical grinding. No anomaly is detected around 110 K in the curves $M = f(T)$ of to the ground samples (Fig. 4). The shape of these curves is strongly dependent to the speed of the milling. The magnetization of the sample ground at 200 rpm shows two ferromagnetic transitions at 95(3) and 70(3) K, according to the derivative curve $\delta M/\delta T = f(T)$. With such milling conditions, the sample is not chemically homogeneous and this could be the origin of the observed magnetic behaviour. On the contrary, only a single ferromagnetic transition is detected at $T_C = 113(5)$ and 110(5) K, respectively, for the samples ground at 250 and 300 rpm. In other words, the mechanical grinding favours the occurrence of a ferromagnetic character for $GdMn_2$. We note that the magnetization measured at 4.2 K for the ground samples which is always higher than that determined for the initial one, reflects an enhancement of the ferromagnetic behaviour. But the decrease of this magnetization with increasing speed grinding could be due to a further decrease of the size of the crystallites.

Let us note that the ferromagnetic transition, observed for sample ground at 300 rpm, is very broad. It spreads out on several degrees K. Also, the magnetization of this sample is practically constant below 80 K. In order to obtain more information on this ground sample, we have performed ac-magnetic susceptibility measurements without an external $\mu_0 H_{DC}$ magnetic field. Fig. 5 compares the thermal dependence of the real χ' and imaginary χ'' parts of the ac-magnetic susceptibility of $GdMn_2$ before and after grinding at 300 rpm. The $\chi' = f(T)$ curve of the initial sample confirms the two magnetic transitions of

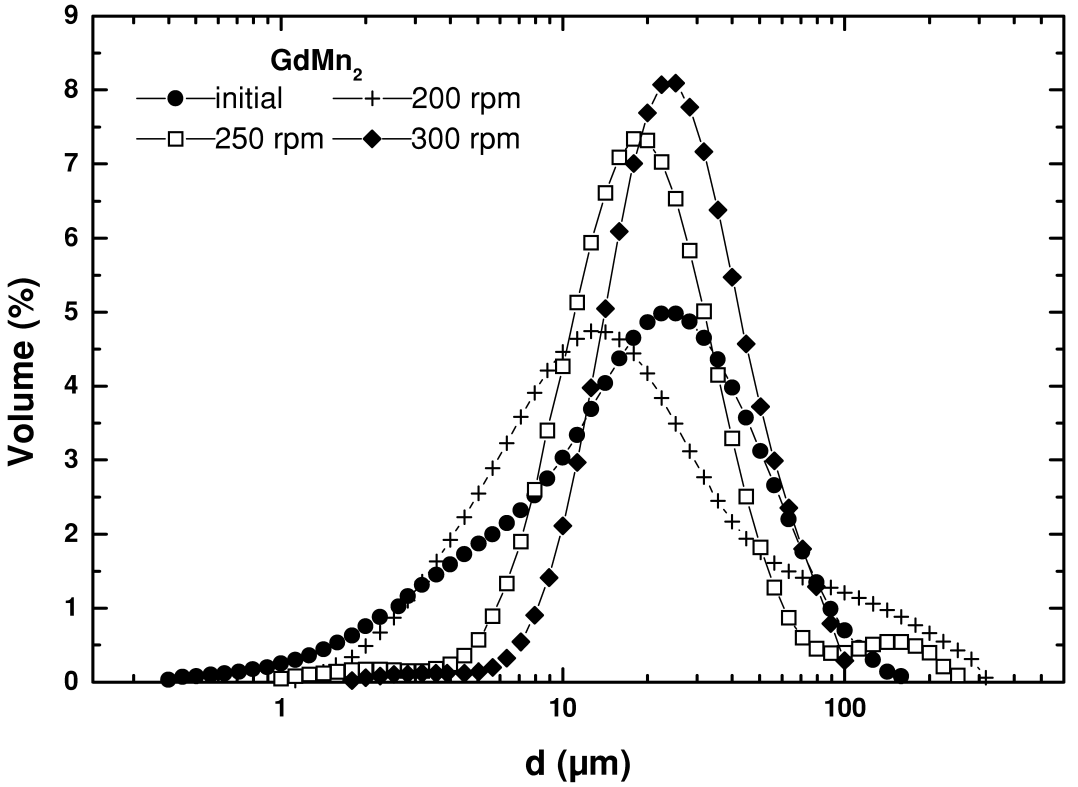

Fig. 3. Particles size distribution of the $GdMn_2$ sample before (initial) and after mechanical grinding at various rotation speeds.

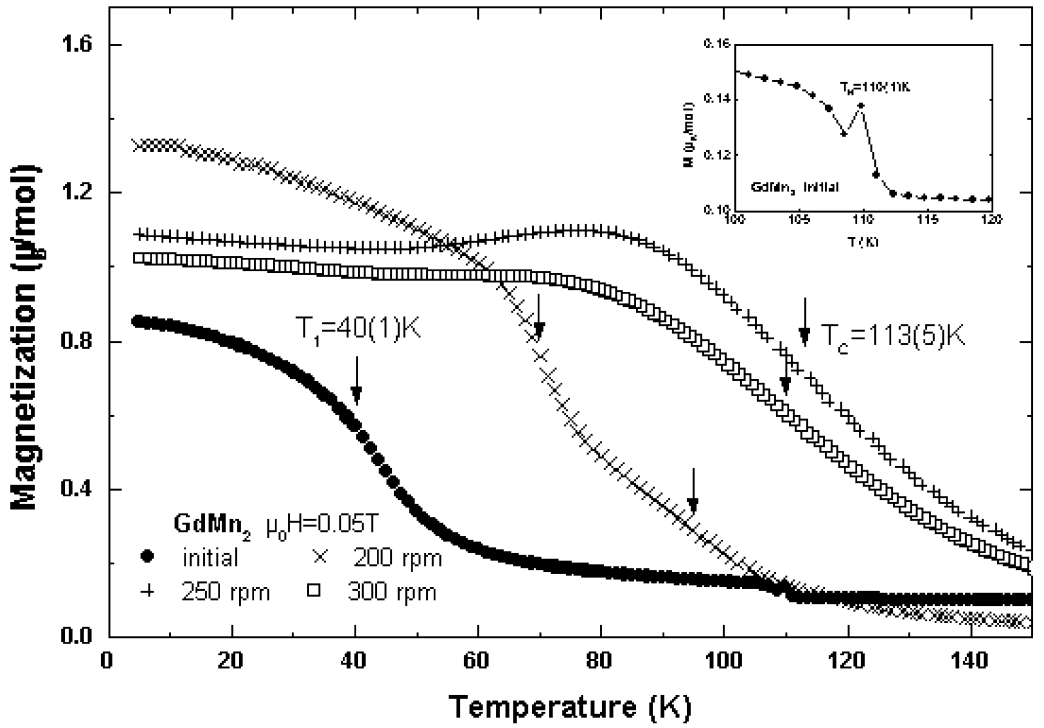

Fig. 4. Temperature dependence of magnetization, measured in an applied field of $\mu_0 H = 0.05$ T, of $GdMn_2$ milled at various speeds.

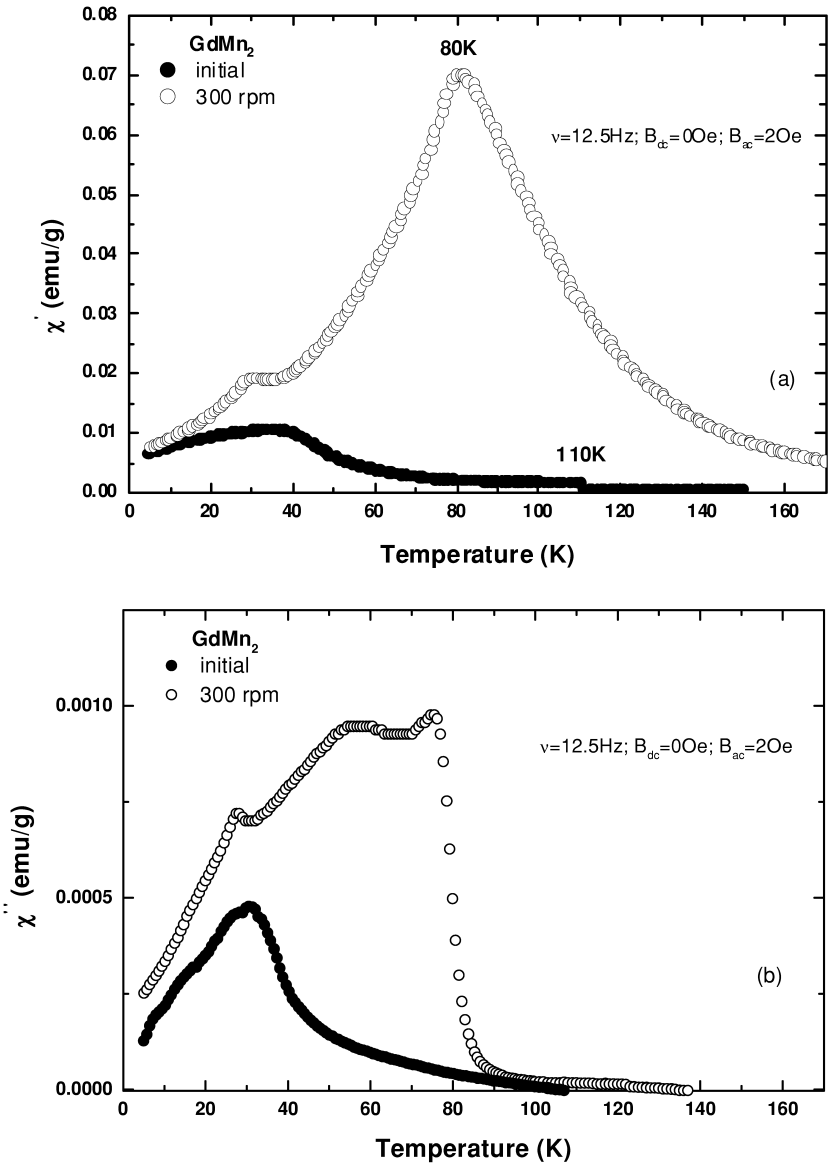

Fig. 5. Temperature dependence of real (a) and imaginary (b) part of the ac-magnetic susceptibility of $GdMn_2$ before (initial) and after mechanical grinding at 300 rpm as rotation speed.

$GdMn_2$: (i) a small increase near 110(1) K, associated with the absence of an anomaly in the $\chi'' = f(T)$ curve, characterizes the occurrence of the antiferromagnetic ordering; (ii) a small and large peak around 35–40 K accompanied by a similar anomaly in the $\chi'' = f(T)$ curve (Fig. 5a) which reflects energy losses in the magnetically ordered state of $GdMn_2$, is presumably connected with domain effects appearing below T_1 in the ferromagnetic state of this intermetallic. On the contrary, for the sample ground at 300 rpm, a well-defined strong peak is detected around 80 K in the $\chi' = f(T)$ curve. At the same temperature, the $\chi'' = f(T)$ curve exhibits a peak. These results agree with the ferromagnetic behaviour of the ground $GdMn_2$ sample.

Fig. 6 shows the isothermal dependence of the magnetization (M) of the ground $GdMn_2$ sample (300 rpm) as a function of applied field. The curve $M = f(\mu_0 H)$ characterizes a compound exhibiting a spontaneous magnetization; at 25 K and $\mu_0 H = 4$ T, M takes a value close to 3.8 μ_B/mol, clearly lower than that expected for Gd^{3+} ion (7 μ_B/mol). The Curie temperature T_C of this sample was estimated from the Arrott's plot presented in Fig. 7. (For this method, the linear curves $M^2 = a(\mu_0 H/M) + b$ indicate a spontaneous magnetization for temperatures below T_C [11].) It can be seen from the data given in Fig. 7 that $T_C \cong 105(5)$ K; this value agrees well with that determined above (Fig. 4) from the magnetization measurements versus temperature.

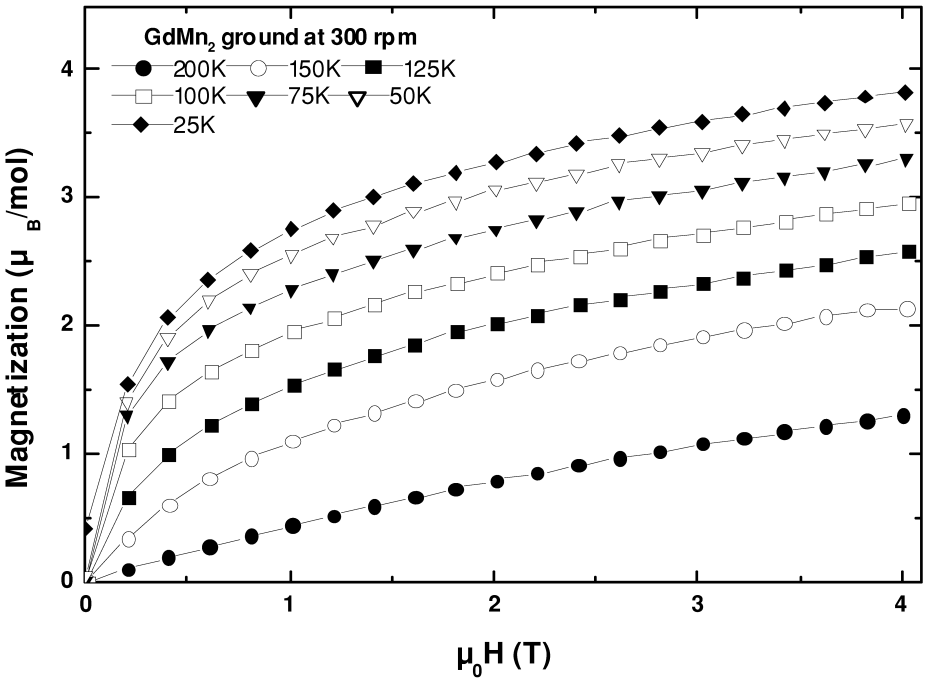

Fig. 6. Field dependence of the magnetization of $GdMn_2$ after mechanical grinding at 300 rpm as rotation speed.

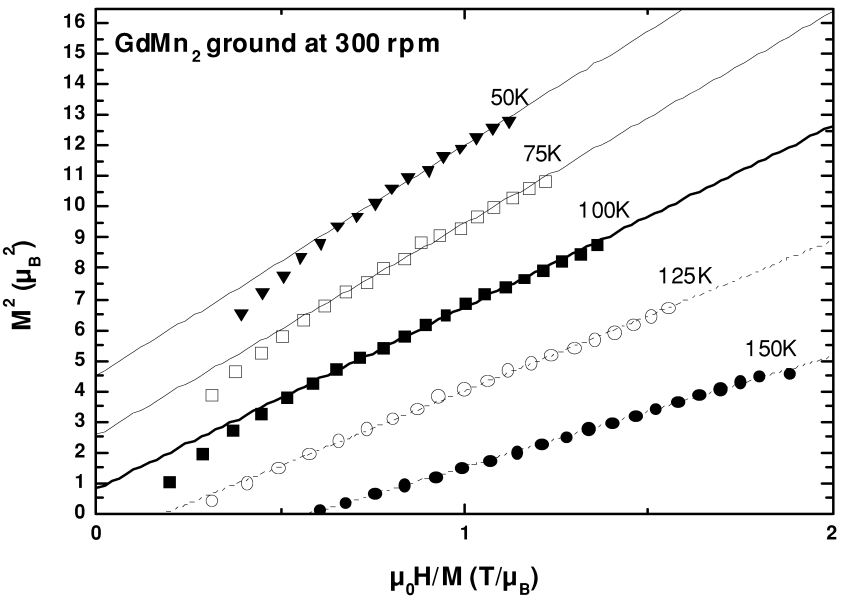

Fig. 7. Arrott plots for $GdMn_2$ after mechanical grinding at 300 rpm.

4. Conclusion

Mechanical grinding of the cubic $GdMn_2$ compound modifies strongly its magnetic properties. After grinding at high speed (300 rpm), this sample exhibits a ferro-ferrimagnetic behaviour below $T_C \cong 105(5)$ K. A similar result is obtained by application of pressure on $GdMn_2$. Mechanical grinding allows to stabilize a new phase having magnetic properties comparable to that of the high pressure form of $GdMn_2$.

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