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Mechanically induced structural and magnetic changes in the $GdAl_2$ Laves phase

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Changes of the structure and magnetic behavior of the $GdAl_2$ Laves phase by high-energy ball milling were followed by x-ray diffraction, ac magnetic susceptibility, and dc magnetization measurements. The starting compound crystallizes in the cubic $MgCu_2$ structure and is a ferromagnet at lower temperatures with a Curie temperature of about 170 K. Upon mechanical milling, the ordered $GdAl_2$ compound is found to become atomically disordered nanocrystalline material. Atomic disorder in $GdAl_2$ is evidenced by the disappearance of a number of x-ray diffraction peaks, the decrease of lattice parameter, the increase of lattice strain, and the drastic changes of high-field magnetization curve at 4.2 K and of the nature of magnetic ordering upon milling. On the basis of experimental observations, a special type of atomic disorder namely *quadruple-defect disorder* is suggested. A constant average-crystallite size of about 21 nm is found after relatively short periods of milling. The material remains in the same crystalline structure as the starting compound even after prolonged periods of milling. While the Curie temperature of $GdAl_2$ is slightly decreased by milling, another magnetic phase is detected with a magnetic ordering temperature of about 45 K during the intermediate stage of milling. This magnetic phase has been proved to be a spin-glass phase [Zhou and Bakker, Phys. Rev. Lett. **73**, 344 (1994)]. With increasing milling time, both the fraction of the spin-glass phase and its freezing temperature T_f increase, while the amount of ferromagnetic phase decreases. After long-period milling the original ferromagnetic phase disappears and the material completely becomes the spin-glass phase with a final T_f of 65 K. Therefore, by mechanical milling well-defined nanocrystalline spin glass is created. The appearance of this spin-glass phase is due to accumulation of quadruple-defect disordering in the lattice of the $GdAl_2$ Laves phase. The importance of using magnetic measurements as a structural probe is emphasized.

I. INTRODUCTION

Mechanical milling in a high-energy ball mill has attracted much interest in recent years since it can be used as a nonequilibrium processing tool. It has been realized that ball milling of crystalline intermetallic compounds (mechanical milling), or of crystalline elemental powder mixtures (mechanical alloying), can be used to synthesize various metastable structures. Typical examples of those structures are amorphous materials,[1–5] crystalline phases existing in the phase diagram at higher temperatures,[5,6] extended solid solutions,[7] solid solutions of immiscible systems,[8] nanocrystalline materials,[9] and quasicrystalline materials.[10] Very recently, a number of spin glasses has been discovered in mechanically milled materials.[11–19] These materials are amorphous Co_2Ge, atomically disordered crystalline $GdAl_2$, and ball-milled crystalline CoZr and amorphous CoZr. Both unmilled Co_2Ge and $GdAl_2$ are ferromagnets at low temperatures, while unmilled CoZr is a paramagnet down to 4.2 K. The common feature of these spin-glass materials is that all are *binary* alloys with a *rather high concentration of the magnetic component* (Co or Gd). The discovery of these spin glasses is by no means trivial because they not only represent new classes of spin-glass materials but also demonstrate that mechanical milling is an effective technique to synthesize various magnetic materials such as spin glasses. Thus this discovery brings more physics in the "ball milling community" and should be considered as a magnetic pendant of the structural amorphization by ball milling. The first spin-glass phase discovered in ball-milled materials is amorphous Co_2Ge. This phase could not be obtained by traditional melt spinning.[11,12] In order to assess the reproducibility of synthesizing spin-glass phases by mechanical milling, the intermetallic compound $GdAl_2$ was studied upon milling. The compound $GdAl_2$ was chosen because amorphous $GdAl_2$ obtained by sputtering is a spin-glass phase.[20] This implies that ball milling of the compound $GdAl_2$ could also result in amorphization and thus a spin-glass phase. Another aim is to emphasize that the magnetic measurement is a powerful structural probe to monitor nonequilibrium processing such as ball milling. Since the magnetic ordering temperature (Curie temperature) of this compound is lower than room temperature [about 170 K (Ref. 21)], one can study the atomic disordering in this compound by measuring the change of magnetic ordering temperature upon milling, without destroying the metastable states. It turned out that the compound $GdAl_2$ does not transform to the amorphous state even after more than 1000 h of milling but that the material milled for long periods does behave as a spin glass. The spin-glass character of these ball-milled materials has been proved by a number of typical experiments and the results obtained on the sample milled for 1000 h, representative of spin-glass material, were recently reported in Ref. 13. In the present paper, we report mainly on the studies of the changes of structural and magnetic behavior of $GdAl_2$ during mechanical milling.

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II. EXPERIMENTAL TECHNIQUES

The intermetallic compound $GdAl_2$ was obtained by arc melting of weighed amounts of pure gadolinium and aluminum in a purified argon atmosphere. Arc melting was repeated at least four times in order to obtain a homogeneous sample. The arc-melted button was crushed to powder and annealed at 800 °C for two days. The x-ray-diffraction pattern of the annealed sample shows single phase material with the cubic $MgCu_2$ structure. Mechanical milling was carried out in a hardened steel vacuum vial (inner diameter 6.5 cm) with a tungsten carbide bottom. Inside the vial, a hardened steel ball with a diameter of 6 cm was kept in motion by a vibrating frame (Fritsch: Pulverisette 0), upon which the vial was mounted. In order to prevent reactions with oxygen or nitrogen, the milling was performed under continuous pumping. During the milling the vacuum was kept at a level of about 10^{-6} Torr. The starting amount of material was a few grams. X-ray-diffraction powders were taken from the samples milled for different periods and after x-ray diffraction the powder was used for magnetic measurements.

The x-ray-diffraction patterns were taken in a Philips diffractometer with vertical goniometer using $CuK\alpha$ radiation. The lattice parameter was calculated from x-ray-diffraction patterns. For an accurate calculation of the lattice parameter, the powder samples for x-ray measurements were mixed with silicon as a standard. The high-field magnetization measurements were performed at 4.2 K in the Amsterdam High Field Installation[22] in which magnetic fields up to 40 T can be generated in a semicontinuous way. A stepwise field profile up to 21 T (one up to 35 T) was used. The sensitivity of this magnetometer is about 10^{-5} A m^2. The ac susceptibility measurement was performed in self-designed equipment.[12] The low dc-field magnetization measurements were carried out in a self-constructed magnetometer. The sensitivity of the magnetometer is better than 10^{-5} A m^2.

III. RESULTS AND INTERPRETATION

A. Structural changes

Figure 1 shows typical x-ray-diffraction patterns of $GdAl_2$ milled for various periods. In agreement with Ref. 23, all reflections of the starting compound (the curve 0 h) can be identified to belong to one single phase having the ordered cubic $MgCu_2$ structure ($C15$, Laves phase) with space group $Fd3m$. All reflections are indexed in Fig. 1. During ball milling the intensity of all reflections decreases gradually with milling time. Meanwhile, the width of the diffraction peaks increases upon milling. After 80 h of milling, some of the low-intensity reflections, e.g., the (622), (444), and (551) reflections, disappear. After 600 h of milling, the relatively strong reflections, e.g., the (222) and (531) reflections, disappear. Upon further milling, a continued decrease of the diffraction intensity is observed. After 1000 h of milling, the reflections (400) and (331) disappear and the other lines broaden further. After further milling, no measurable changes in the x-ray-diffraction pattern are found. The material can still be identified as crystalline with $MgCu_2$ structure even after 1210 h of milling. No evidence for amorphization is obtained. The absence of a number of reflections strongly indicates that atomic (chemical) disorder is generated in $GdAl_2$ by mechanical milling.

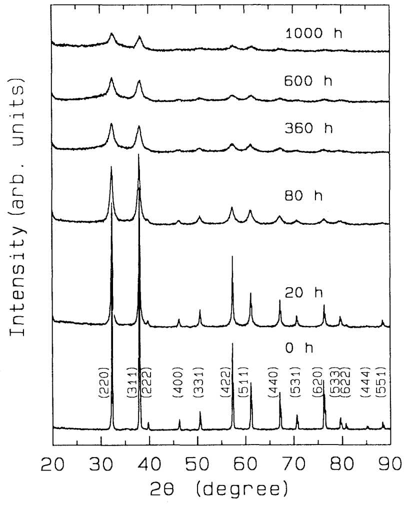

FIG. 1. X-ray-diffraction patterns of $GdAl_2$ after various periods of milling.

Figure 2 displays the relative change of lattice parameter of $GdAl_2$ vs milling time. It turns out that the lattice parameter of $GdAl_2$ decreases monotonously with increasing milling time until 1000 h of milling and tends to become constant upon further milling. The maximum relative change is -0.56%. The contraction of the unit cell of $GdAl_2$ after ball milling suggests that atomic disorder is induced in $GdAl_2$ lattice combined with many vacancies. This could point in the direction of the gen-

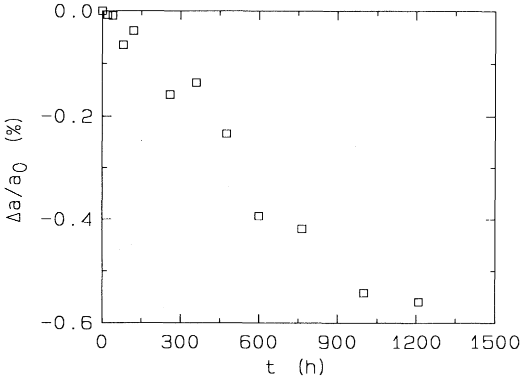

FIG. 2. Relative change of the lattice parameter of $GdAl_2$ as a function of milling time.

eration of a special type of atomic disorder, which will be discussed in details in Sec. IV.

As pointed out in previous investigations,[19,24–26] the major sources for line broadening from mechanically milled materials are (1) small crystallite size (coherent domains) and (2) strains and distortions within the crystallites. Using Langford's Voigt-deconvolution method the size broadening and the internal-strain broadening can be separated (see Ref. 24 for details). The average crystallite size and the relative strain were thus calculated from the x-ray-diffraction patterns. During evaluation, the (220) and (422) reflections were used, while the x-ray-diffraction pattern of the starting compounds was used as a standard to correct for the instrumental broadening. The obtained average crystallite size and relative strain are plotted in Fig. 3 as a function of milling time. The average crystallite size decreases abruptly with increasing milling time up to 120 h of milling. Upon further milling, it tends to become constant at a value of about 21 nm. So, during mechanical milling, $GdAl_2$ becomes nanocrystalline. Simultaneously, the relative strain increases continuously with increasing milling time up to 600 h, with a final value of about 1.5%. Such a large increase of the relative strain also suggest the introduction of atomic disorder in $GdAl_2$ by mechanical milling. It is very interesting to note that the variation of both lattice strain and lattice parameter is quite different from that of the crystallite size. The crystallite size tends to become constant after relative short period of milling, whereas both lattice parameter and lattice strain become constant after much longer periods of milling. This is very important for the discussion in Sec. IV because both lattice parameter and lattice strain are intrinsic parameters of $GdAl_2$, which directly reflect the configuration of the local environment in the $GdAl_2$ lattice.

B. Magnetic changes

Typical high-field magnetization curves up to 21 T at 4.2 K are presented in Fig. 4. A field profile up to 35 T was applied for the sample milled for 1210 h. In the starting compound (labeled 0 h), a field-induced transition at about 2.5 T is observed. After that, the magnetization saturates by further increasing the external field. The observation of a field-induced transition in the starting $GdAl_2$ compound indicates that a nonlinear structure of magnetic moments exists in the compound. This structure is already broken in a relatively low field and the moments become perfectly ferromagnetically aligned. The saturation moment is about 7.4 μ_B/Gd atom which exceeds the free-ion saturation moment of 7 μ_B/Gd atom. At present, this discrepancy is not understood. $GdAl_2$ is a line compound and thus it cannot be due to an off-stoichiometric composition. The excess moment can partially be due to the polarization of the conduction electrons. Upon mechanical milling, both the magnetization at 4.2 K and in particular the magnetic susceptibility change drastically. The high-field susceptibility increases strongly with increasing milling time. For the samples milled for 80 h or longer, the magnetization does not saturate in a field of 21 T. For the sample milled for 1210 h, even in a field of 35 T the magnetization does not saturate. In order to better compare the milling-time dependence of magnetization at 4.2 K, the magnetization of various samples at both 1.3 T (lowest field applied) and 21 T (highest field applied for most of the samples) is plotted as a function of milling time in Fig. 5. The magnetization

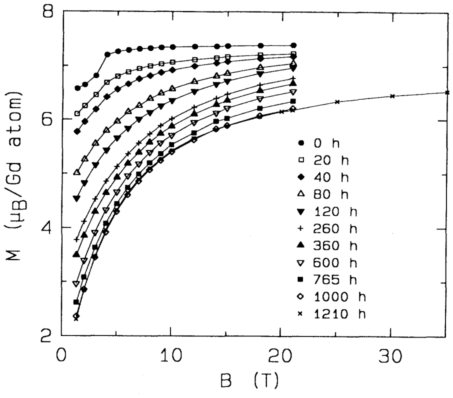

FIG. 4. High-field magnetization curves of $GdAl_2$ at 4.2 K after various periods of milling.

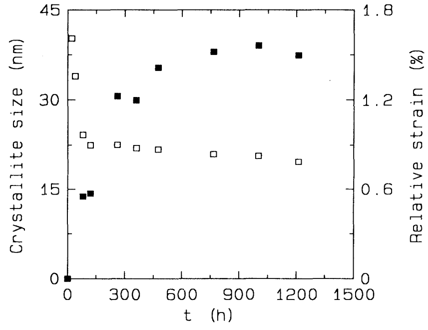

FIG. 3. The average crystallite size (open squares and left-hand-side scale) and the relative strain (filled squares and right-hand-side scale) of $GdAl_2$ as a function of milling time.

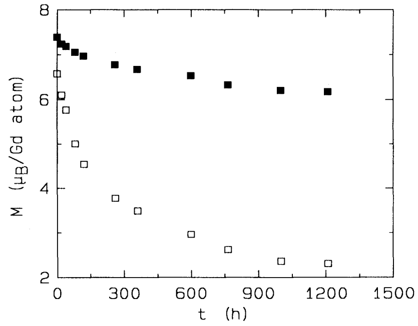

FIG. 5. Magnetization of $GdAl_2$ at 4.2 K and 1.3 T (open squares) and 21 T (filled squares) as a function of milling time.

at both 1.3 and 21 T decreases with increasing milling time up to 1000 h and then tends to become constant upon further milling. But, the change of the low-field magnetization (at 1.3 T) is much more rapid than that of the high-field magnetization (at 21 T) and thus the magnetization difference between 1.3 and 21 T for the same sample increases with increasing milling time. Since the Gd atom is a 4*f* element and thus the absolute value of its magnetic moment can hardly be changed by changing the local environment of a Gd atom, the observed decrease of magnetization of $GdAl_2$ upon milling cannot be attributed to the change of the value of Gd moment by atomic disorder. However, ball-milling-induced atomic disorder will certainly change the number of nearest Gd-Gd neighbors and the relative distance between Gd atoms. This will probably cause a change of the direction of Gd moment from the originally parallel alignment (ferromagnet) to a randomly distributed configuration. Thus, in ball-milled $GdAl_2$, an antiferromagnetic interaction becomes possible. The ball-milled materials are then composed of the mixed interactions of ferromagnetic and antiferromagnetic. With increasing milling time, the amount of atomic disorder is increased, thus the fraction of antiferromagnetic interaction in $GdAl_2$ may be increased. Therefore, the magnetization, in particular the low-field magnetization, of $GdAl_2$ at 4.2 K decreases with increasing milling time. Apparently, the applied field of 21 T is too low to align all the randomly distributed Gd moments or spins in ball-milled $GdAl_2$ in the same direction as the external field. Therefore, a smaller value of the magnetization at 21 T is observed. If the field applied is high enough, it may be expected that the magnetization of all ball-milled $GdAl_2$ would reach the same value as that of unmilled compound. The randomness of the Gd-moment directions caused by milling-induced atomic disorder is essential for the formation of spin-glass character in ball-milled $GdAl_2$. From the fact that both the high-field magnetic susceptibilities and the magnetization of the samples milled for 1000 and 1210 h are the same, it is concluded that the material reaches a final state after milling for 1000 h or longer. This is further supported by the results obtained from the ac susceptibility measurements, which are shown in the following.

The temperature dependence of the ac susceptibility χ_{ac} (real part) of $GdAl_2$ after various periods of milling is given in Figs. 6 and 7. In the starting compound (0 h), a ferromagnetic transition is evident upon cooling to low temperatures. The Curie temperature T_C is about 170 K, which is in good agreement with the T_C value reported by Buschow.[21] This transition is very sensitive to mechanical milling. The transition temperature decreases upon milling and the transition broadens. Moreover, the intensity of the transition decreases with milling time. These phenomena are attributed to the introduction of defects, e.g., atomic disorder and mechanical deformation. The observation that the intensity of the transition decreases with increasing milling time indicates that the amount of the ferromagnetic phase is reduced upon milling. After 475 h of milling, T_C is decreased by a few degrees and after 600 h of milling the ferromagnetic transition has disappeared completely. On the other hand, starting from 60 h of milling, another anomaly at a quite different temperature, namely at about 45 K, is detected, indicating the formation of a magnetic phase. Both the peak temperature T_f and the transition intensity increase with milling time, indicating the homogenization and the increase of the amount of this magnetic phase. In Fig. 8 the transition temperature T_f is plotted as a function of milling time. It is seen that T_f increases monotonously with milling time up to 1000 h and tends to become constant at a value of about 65 K upon further

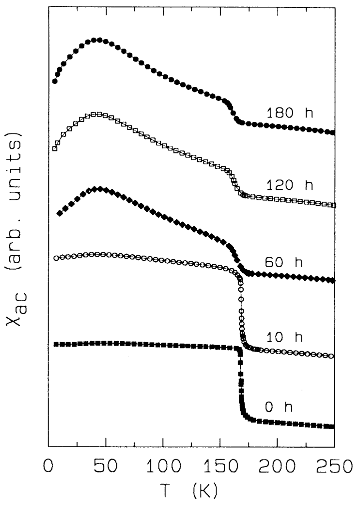

FIG. 6. Temperature dependence of the ac susceptibility of $GdAl_2$ after milling up to 180 h in an external field of 1.2 Oe with a frequency of 109 Hz.

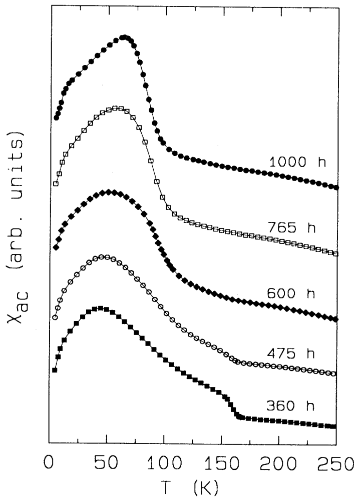

FIG. 7. Temperature dependence of the ac susceptibility of $GdAl_2$ after milling longer than 180 h in an external field of 1.2 Oe with a frequency of 109 Hz.

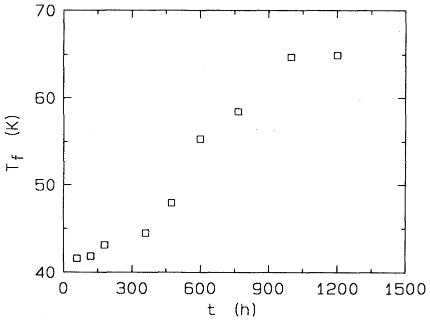

FIG. 8. Freezing temperature T_f of $GdAl_2$ as a function of milling time.

milling. The tendency of the change of T_f with milling time is very similar to that of the lattice parameter (Fig. 2). In fact, the original ferroparamagnetic transition disappears after 600 h of milling, indicating that the material has completely transformed to this magnetic phase. This magnetic phase turns out to be a spin-glass phase and not a ferromagnet. The evidence for this has been given in Ref. 13 and some typical results will also be presented later. The above observation is consistent with x-ray-diffraction results and gives more insight in the structural changes during the intermediate stage of milling.

C. Spin-glass behavior of mechanically milled crystalline $GdAl_2$

In previous sections, it was shown that upon mechanical milling ferromagnetic $GdAl_2$ with a Curie temperature of about 170 K transforms to a magnetic phase with a magnetic ordering temperature of 65 K. This magnetic phase has been proved to be a spin-glass phase.[13] The characteristic features of spin glasses as defined in Refs. 27–30 are observed, i.e., (a) the sharp cusps at the freezing temperature T_f in both ac and dc magnetic susceptibility vs temperature curves and their peculiar sensitivity to the external-magnetic field; (b) the irreversibility, i.e., the difference in value and shape between the magnetization vs temperature curves after zero-field cooling (ZFC) and field cooling (FC) at temperatures below T_f; and (c) the displacement of the FC magnetization curve relative to ZFC curve and the corresponding remanence in the FC curve at low temperatures. Since all samples milled for 1000 h or longer exhibit the same behavior, the sample milled for 1000 h, as representative of spin-glass material, has been extensively studied.[13] This material is referred to as mm-$GdAl_2$ (mechanically milled $GdAl_2$). Here we present some typical results.

In Fig. 9, the temperature dependence of the ac susceptibility χ_{ac} (real part) of mm-$GdAl_2$ is given. The measurements were performed in different ac fields from 0.1 to 150 Oe. The frequency used was 109 Hz. An asymmetric sharp cusp at 65 K (the freezing temperature T_f) is observed when the external field is low, e.g., 0.1 Oe. This cusp loses its sharpness and becomes a rounded maximum upon increase of the external field. Both peak temperature and peak intensity decrease with increasing field. These observations, i.e., the changes with external field of the shape, the peak temperature and the height of the transition are very similar to those observed for amorphous Co_2Ge (Ref. 12) and for the prototype spin glass FeAu,[27,30] and were confirmed by the results of dc low-field susceptibility measurements.[13] The irreversibility at temperatures below T_f is also observed in mm-$GdAl_2$. This is illustrated in Fig. 10, where magnetization vs temperature curves are given, measured in a field

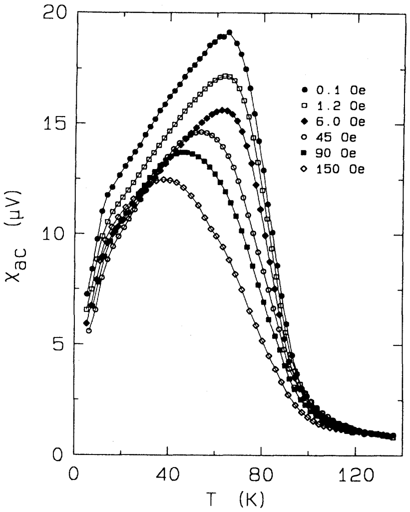

FIG. 9. Temperature dependence of the ac susceptibility (real part) of $GdAl_2$ after 1000 h of milling in various external fields and a frequency of 109 Hz.

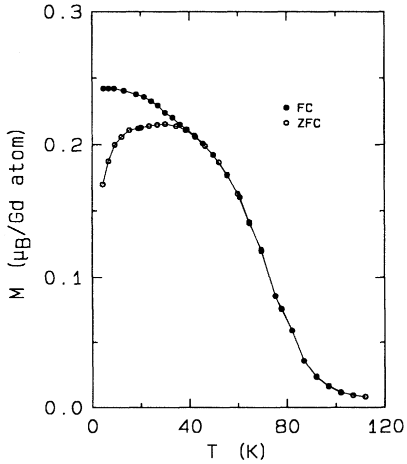

FIG. 10. Temperature dependence of the magnetization of $GdAl_2$ milled for 1000 h after zero-field cooling (ZFC) and field cooling (FC) in a field of 220 Oe.

of 220 Oe after zero-field cooling (ZFC) and field cooling (FC). Remarkable are the features at and below T_f. The FC magnetization (filled circles) decreases gradually with increasing temperature but to a great extent independent of time. FC followed by field heating shows reversibility. In contrast, the ZFC magnetization (open circles) increases with temperature until T_f, where the two curves coincide. Moreover, the ZFC magnetization is irreversible. These observations are similar to those observed for amorphous Co_2Ge (Ref. 12). Thus the dc field, when applied below T_f, creates a metastable and irreversible state in mm-$GdAl_2$. A clear displacement of the FC magnetization curve relative to the ZFC curve in mm-$GdAl_2$ is observed.[13] Thus mm-$GdAl_2$ undergoes a single paramagnetic to spin-glass transition with a freezing temperature of about 65 K upon cooling from room temperature to lower temperatures. The freezing temperature is shifted to lower temperature with increasing magnetic field. The T_f vs B_{ext} phase diagram has been established.[13]

In order to check the influence of impurities such as iron, which may be introduced during ball milling, we also measured the magnetization curves of some typical ball-milled samples after annealing. It turned out that both the magnetization and the magnetic susceptibility of the annealed samples are quite close to those of the unmilled sample. Thus the change of the magnetic behavior in $GdAl_2$ is really resulting from atomic disorder in $GdAl_2$ lattice, while the influence of impurity Fe is negligible.

IV. DISCUSSION

From the above, it is clear that upon mechanical milling atomic disorder is created in the $GdAl_2$ lattice and the crystallite size is reduced to a nanometer-sized scale. The absence of a large number of x-ray reflections, the large increase of the relative strain, and the decrease of lattice parameter strongly suggest the generation of atomic disorder. As a significant consequence of atomic disorder, the high-field magnetic susceptibility strongly increases and the magnetization in particular the low-field magnetization at 4.2 K and Curie temperature decrease, and eventually the material completely transforms to a spin glass from the ferromagnetic $GdAl_2$. The results of ac susceptibility together with those of high-field magnetization and of x-ray diffraction suggest that the milling process of $GdAl_2$ can be considered as consisting of three stages.

The first stage is for a milling time shorter than 60 h. In this stage, a single transition resulting from the original paraferromagnetic transition of $GdAl_2$ is observed in the ac susceptibility vs temperature curves. But the transition becomes broader and the transition temperature (Curie temperature T_C) is lowered slightly upon milling. The lattice parameter decreases slightly with increasing milling time, while the crystallite size decreases drastically. Thus the material is heavily deformed during this stage of milling accompanied by a small degree of disorder. The broadening of the paraferromagnetic transition is attributed to the deformation-induced anisotropy and inhomogeneous defect concentration (e.g., dislocations). The decrease of the Curie temperature is due to both the milling-induced atomic disorder and the severe deformation. The effect of mechanical deformation on the Curie temperature of a ferromagnet has also been studied by Griffith *et al.*[31] and Pilipowicz *et al.*[32] If we define S_0 as the Bragg-Williams long-range-order (LRO) parameter of the as-prepared $GdAl_2$ and S_1 as the LRO parameter of the materials milled in this stage, then S_1 is smaller than S_0.

The second stage is for milling periods between 60 and 600 h. In this stage, the material undergoes an intrinsic transformation from the ferromagnetic phase to a spin-glass magnetic phase. The spin-glass phase starts to appear after 60 h of milling, indicated by a peaklike transition at about 45 K (freezing temperature T_f) in the ac susceptibility vs temperature curve. This phase develops continuously upon further milling. Both the transition intensity and the peak temperature increase with increasing milling time, suggesting an increased fraction of this magnetic phase and a continuous change of atomic arrangement in this phase. Meanwhile, the original paraferromagnetic transition becomes weaker and broader, and the Curie temperature is slightly decreased, with increasing milling time. This means that the amount of the original ferromagnetic phase is decreased while it is further deformed and disordered. That the magnetic ordering temperature of the spin-glass phase is quite different from that of the ferromagnetic phase suggests that both disordered states are very different. Apparently, the spin-glass phase is (chemically) atomically more disordered than the ferromagnetic phase because the T_f of the spin-glass phase is more than 100 K lower than the T_C of the ferromagnet. This means that if we define S_2 as the LRO parameter of the spin-glass phase, then S_2 is much smaller than S_1. This is reflected by the fact that both the lattice parameter and the lattice strain vary significantly, strongly indicating that a large degree of atomic disorder is generated during this stage of milling. Thus the coexistence of both the paraferromagnetic transition and the para-spin-glass transition shows that the material is composed of two materials with quite different structural states represented by the LRO parameter S_1 and S_2, respectively. However, x-ray diffraction does not give such information because it measures the average. The slight decrease of T_C and the increase of T_f and the broad character of both transitions reflect that both S_1 and S_2 values have a certain range. After 600 h of milling, the ferromagnetic phase disappears and the material completely transforms to the spin-glass phase. Thus milling of $GdAl_2$ induced an intrinsic transition from a ferromagnetic phase to a spin-glass phase as a significant consequence of (chemical) atomic disorder in the $GdAl_2$ lattice. It must be emphasized that the refinement of the crystallite size does not really contribute to this transition, because the crystallite size already becomes constant after 120 h of milling whereas the transformation is continuously occurring upon further milling up to 600 h. Apparently, the driving force is not the refinement of crystallites but the atomic disorder.

The type of atomic disorder in $GdAl_2$ is probably similar to that in $B2$ CoGa (Ref. 33) and CoAl.[34] In both CoGa and CoAl, a special type of disorder so-called triple-defect disorder is induced by milling. A triple defect consists of one antisite Co atom combined with two vacancies (on Co sublattice). This means that Co atoms are able to substitute on the "wrong" sublattice (Ga or Al sublattice) but that the Ga or Al atoms are not able to substitute on the wrong sublattice (here Co sublattice). Possibly, this is due to the large difference in atomic size between Ga or Al atoms and Co atoms. The nonmagnetic Ga and Al atoms are bigger than the magnetic Co atoms. Triple-defect disordering results in an increase of the magnetization and in a decrease of the lattice parameter. However, it does not result in a phase transformation to the amorphous state or solid solution. In the present case, the magnetic Gd atoms are significantly larger than the Al atoms. This could mean that the Al atoms are able to substitute on the Gd sublattice, but that the Gd atoms are not able to substitute on the Al sublattice. If such disorder really occurs in $GdAl_2$ upon milling, an antisite Al atom on the Gd sublattice will leave three vacancies on the Al sublattice. The reason is that both sublattices should contain an equal number of lattice sites. Thus we call this type of disorder "quadruple-defect disorder." Quadruple-defect disordering will result in a decrease of the number of Gd-Gd nearest neighbors and an increase of the relative distance between Gd atoms. This will lead to a decrease of the Gd-Gd exchange interaction and thus the magnetic-ordering temperature. This is fully corroborated by the experiment (Figs. 6 and 7). As expected, quadruple-defect disorder did not lead to a phase transformation to the amorphous state or a solid solution. Another consequence of such a disorder is the decrease of lattice parameter. This is indeed experimentally observed (Fig. 2).

Recently, Foley, Thoma, and Perepezko[35] have obtained the supersaturated YAl_2 Laves phase by rapid quenching, with a remarkable composition range from 18.1 to 43.8 at. % Y. This compound is very similar to $GdAl_2$ in the equilibrium phase diagrams. That is, both are line compounds and have C15 $MgCu_2$-type structure. It was found that the lattice parameter of YAl_2 decreases with increasing Al concentration. A change of the slope at the stoichiometric composition is observed. On the Al-rich side of stoichiometry, the slope is steeper than that observed on the Y-rich side of stoichiometry. This was explained as due to a different defect mechanism on either side of stoichiometry. That is, antisite substitution is likely on the Al-rich side of stoichiometry and vacancy defects may develop in the Y-rich alloy composition. Although further work is apparently required to confirm the defect mechanisms in YAl_2, their results indicate that by nonequilibrium processing techniques it is possible to create atomic disorder in the lattice of a Laves phase, which is a line compound. So, it is not surprising that we observe atomic disorder in $GdAl_2$ during mechanical milling. We believe that the same type of disorder as in our ball-milled $GdAl_2$, i.e., quadruple-defect disorder, appears in quenched YAl_2. It seems that rapid quenching experiments on $GdAl_2$ would be interesting.

The third stage is for milling periods from 600 to 1210 h. In this stage, the material consists of a single spin-glass magnetic phase but its magnetic transition temperature and shape in ac susceptibility vs temperature curves are still changing upon further milling until 1000 h. This means that a local rearrangement of Gd atoms is continuously taking place. This is further evidenced by the continuous change of lattice parameter. It is interesting that the transition shape becomes sharper and the peak temperature is shifted to higher temperature. This may mean a rearrangement of the Gd atoms in such a way that the exchange interaction becomes stronger and that the material becomes a homogeneous material. By more carefully inspecting Figs. 2, 3, and 8, where the lattice parameter (Δa), lattice strain (LS), and freezing temperature (T_f) are respectively plotted as a function of milling time, one may note that the LS saturates around 600 h while both Δa and T_f continuously change up to 1000 h. In fact, the LS development occurs in the same time interval as the disappearance of the ferromagnetic phase. These observations might indicate that the deformation behavior and the nature of the defects generated in the ferromagnetic phase and the spin-glass are different. In the material, there is LRO but also surely short-range order (SRO). However, at a given value of the LRO parameter, certain SRO configurations representing nearest-neighbor configurations with different free energy can still occur. It could well be that the continuous changes occurring in the spin-glass phase result from changes in the SRO. After milling for 1000 h or longer, all parameters tend to become constants. This means that the material reaches a stationary state and during further milling no net atomic transfer will occur and thus mechanical energy cannot be further stored in the material by continuing milling (since crystallite size has become constant after relative short period of milling, the grain boundaries cannot store more energy upon further milling). Thus it is believed that the material cannot transform to the amorphous state even after milling for a longer time.

Why does the compound $GdAl_2$ not transform to amorphous even after a prolonged period of milling? As argued previously,[5,11] antisite disorder is the prerequisite for the phase transformation to an amorphous state or a solid solution. Antisite disorder means an exchange of the different types of atoms between sublattices. As argued above, it seems not possible to create antisite disorder of both components in $GdAl_2$ because the size difference between Gd and Al atoms is too big. Therefore, $GdAl_2$ could not transform to amorphous state even after prolonged periods of milling. This is consistent with the generation of the quadruple-defect disorder in $GdAl_2$.

Why does the mechanically milled $GdAl_2$ behave as a spin glass? A spin glass is defined as a magnetic system with mixed, i.e., ferro- and antiferromagnetic interactions, which is characterized by a random, yet cooperative freezing of spins at a well-defined temperature T_f

below which a highly irreversible, metastable frozen state occurs *without the usual long-range* spatial magnetic order. So, the most important prerequisites for a spin glass are randomness in either position of the spins or in the signs of the coupling between neighboring spins: ferro- or antiferromagnetic and the site or bond disorder. Apparently, mechanical milling creates quadruple-defect disorder in $GdAl_2$ lattice and thus mixed antiferromagnetic and ferromagnetic interactions, as argued in Sec. III B. As soon as an appropriate ratio of antiferromagnetic and ferromagnetic interactions has been achieved, spin-glass behavior is expected. Therefore, after a long period of milling the material becomes a spin glass. This spin-glass phase is a site-random spin glass.

It is interesting to compare the magnetic behavior of our mm-$GdAl_2$ spin glass with that of amorphous $GdAl_2$ (a-$GdAl_2$, the practical composition was $Gd_{0.37}Al_{0.63}$) film obtained by sputtering.[20] A great similarity is that both mm-$GdAl_2$ and a-$GaAl_2$ are spin-glass phases. However, the freezing temperature T_f of a-$GdAl_2$ (16 K) is quite different from that of the mm-$GdAl_2$ (65 K). This means that mm-$GdAl_2$ represents a new class of spin-glass materials, because it is neither a dilute solution nor amorphous. It is a crystalline intermediate phase, but atomically disordered and so metastable. Apparently, ball milling is a unique technique to create this spin-glass phase in $GdAl_2$. The T_f of mm-$GdAl_2$ is higher than that of a-$GdAl_2$. This could mean that the magnetic cluster sizes in mm-$GdAl_2$ are on the average larger than those in a-$GdAl_2$. This is further reflected in the value of the paramagnetic Curie temperature, which is about 30 K in a-$GdAl_2$ (Ref. 20) and about 84 K in mm-$GdAl_2$ (this value was obtained by extrapolating χ^{-1} against T using the magnetic susceptibility data in the temperature range from 100 K to room temperature). The paramagnetic Curie temperature represents a sum of all the exchange interactions for a completely random alloy. So, ferromagnetic exchange interactions are more probable in mm-$GdAl_2$ than in a-$GdAl_2$. Amorphous $GdAl_2$ is a positional-random spin glass but mm-$GdAl_2$ is a site-random spin glass.

V. CONCLUSIONS

Mechanical milling of the ordered intermetallic compound $GdAl_2$ results in atomic (chemical) disorder but preserves the original crystalline structure. Evidence for atomic disorder is obtained from both x-ray-diffraction and magnetic measurements. The absence of a large number of reflections, the decrease of lattice parameter, and the large increase of lattice strain upon milling strongly suggest the generation of atomic disorder. The high-field magnetic susceptibility increases largely and the magnetization, in particular the low-field magnetization, at 4.2 K and Curie temperature decrease upon milling. Based on the experimental observations, a special type of disorder namely *quadruple-defect disorder* is proposed. The material milled for long periods exhibits a single transition from the paramagnetic to the spin-glass state with a T_f of 65 K, which is lowered with increasing external field. The appearance of the spin-glass magnetic phase is due to accumulation of atomic disordering in the lattice of the $GdAl_2$ Laves phase. So, mechanical milling induces an intrinsic transformation from the ferromagnetic $GdAl_2$ to a spin glass. This means that mechanical milling can create a "pure" spin-glass state even in a crystalline compound with a magnetic element content as high as 33 at. %. Therefore, mechanical milling is a unique nonequilibrium processing technique to synthesize unusual and so far unknown spin-glass materials with a high content of the magnetic element. The importance of the magnetic measurements as a structural probe to monitor the milling process of intermetallic compounds is again emphasized.

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