Influence of Mechanical Milling on Magnetic Properties of Intermetallic Compounds (Overview)

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The influence of mechanical milling on magnetic properties of various types of intermetallic compounds has been extensively investigated. It is established that, on the one hand the measurement of magnetic properties is a very sensitive probe to structural changes of intermetallic compounds during milling, and on the other hand milling may induce in the material unusual and interesting magnetic properties. The results are reviewed. It is generally observed that mechanical milling of an intermetallic compound results in atomic disorder. The disordered materials may remain in the same crystal structure or transform to a different structure, which can be the amorphous structure, a solid solution or a different complex crystalline structure. If the material is crystalline, it becomes always nanocrystalline. The magnetization of various intermetallic compounds after milling was measured at 4.2 K in the Amsterdam High Field Installation in fields up to 21 or 35 T. The high-field magnetization at 4.2 K and the magnetic susceptibility changes usually significantly and sometimes drastically as a consequence of atomic disorder and/or disorder-induced phase transformation. The magnetic ordering temperature was also measured in some compounds. The obtained results turn out to provide precise information about the structural change of a compound in particular during the intermediate stage of milling. Upon disordering or phase transformation, the nature of the magnetic ordering of a compound can be markedly different from its ordered form. This is illustrated by the discovery of two novel binary concentrated spin glasses namely amorphous Co₇Ge and atomically disordered crystalline GdAl₃.

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I. Introduction

In a perfectly ordered intermetallic compound, two or more sublattices can be distinguished. Each sublattice is usually occupied by only one kind of atoms. Mechanical milling in a high-energy ball mill of an ordered compound usually results in atomic disorder. The disordered materials may or may not transform to a different structure, which can be the amorphous structure, a solid solution or a different complex crystalline structure. In an atomically (chemically) disordered compound, the atoms of different types are randomly distributed over the lattice sites. In an ordered compound, where the atomic arrangement is long-range ordered, a number of extra reflections (so-called superlattice reflections) appears in the X-ray or neutron diffraction patterns. The long-range-order (LRO) parameter can thus be derived from the intensity of a superlattice reflection relative to that of a fundamental reflection by

\[
\frac{S}{S_0} = \frac {(I_s/I_0)_{5s}} {(I_s/I_0)_{5s}},
\]

where \((I_s/I_0)_5\) is the intensity of the superlattice reflection relative to that of the fundamental reflection at a value \(S\) of the long-range-order parameter and \(S_0\) is equal to unity for the case of complete order. The LRO parameter varies from \(S=1\) for complete order to \(S=0\) for complete disorder. Therefore, the degree of disorder induced by non-equilibrium processing, such as mechanical milling, can in principle be measured by comparing the intensities of reflections in the diffraction pattern. This technique was used successfully to investigate disordering by milling for example in AlRu, crystallizing in the B2 structure (ordered b.c.c.) and in Ni₃Al, crystallizing in the L1₂ structure (ordered f.c.c.). In both cases the disorder is anti-site disorder of both components, i.e. both atomic species substitute on the 'wrong' sublattices. However, the use of such a diffraction technique is limited. In compounds with a complex structure, for example orthorhombic and hexagonal, the superlattice reflections can hardly be distinguished from fundamental reflections. However, measurements of various physical properties can provide an alternative way to monitor structural changes due to milling. Among other properties, magnetic-property measurements turn out to be particularly effective. These have been successfully used to study disordering and phase transformations by milling in a large number of intermetallic compounds. It is inferred from these investigations that on the one hand, the measurement of magnetic properties provides an important structural-probe tool to monitor the milling process of an intermetallic compound, on the other hand, milling may induce special properties in the material. The experimental results obtained so far are reviewed in the present...
II. B2-Structure Compounds

First, we deal with the B2 structure compounds CoM (M=Zr, Ga, Al)\textsuperscript{13-16}. The B2 structure is cubic as shown in Fig. 1. In this structure, two interpenetrating primitive cubic sublattices can be distinguished indicated as the $\alpha$ and $\beta$ sublattice, which are occupied by Co and M atoms, respectively. In the ordered state, the Co atoms are isolated from one another by non-magnetic M atoms and the material is non-magnetic. Superlattice reflections appear in X-ray diffraction pattern. However, when a Co atom is transferred from the $\alpha$ sublattice to the $\beta$ sublattice, i.e., to the 'wrong' sublattice (anti-site Co atom), it is surrounded by eight nearest-neighbour Co atoms (on the $\alpha$ sublattice) and bears a magnetic moment. The material then becomes magnetic. Such a disordering i.e. a decrease of the long-range-order (LRO) parameter results in a decrease of the intensity of the superlattice reflections relative to the fundamental reflections in the X-ray pattern. Therefore, both magnetic measurements and X-ray diffraction are in principle suitable for studying disordering in compounds with the B2 structure. However, Cho and Koch\textsuperscript{10} found that no appreciable reduction of the LRO parameter of CoZr by milling can be derived from the X-ray patterns before amorphization. This was confirmed by the present authors\textsuperscript{13}. So, it seemed that in this compound atomic disorder does not occur and the grain-boundary energy alone could be high enough to drive the amorphization. However, magnetic measurements clearly showed that as a matter of fact atomic disorder is induced in CoZr before amorphization\textsuperscript{13,14}. Thus, magnetic measurements are more sensitive than X-ray diffraction even in compounds with a relatively simple structure. Representative magnetic data are given in the following.

Figure 2 gives the high-field magnetization curves at 4.2 K of CoZr after various periods of milling\textsuperscript{13,14}. It is clear that both magnetization and magnetic susceptibility of the ball-milled CoZr are quite different from those of the starting compound. The value of the magnetization of CoZr at 4.2 K increases strongly with milling time up to 40 h and decreases by further milling due to amorphization\textsuperscript{13}. It tends to become constant after 160 h of milling, where the amorphization is completed\textsuperscript{13}. The magnetic susceptibility of the amorphous material is somewhat larger than that of the crystalline materials (both unmilled and milled for less than 40 h). Thus, the intersection of the two magnetization curves of the samples milled for 40 and 20 h suggests that amorphization starts at a milling time of 40 h. The measured magnetization is an average of those of the mixed crystalline and amorphous phases. The magnetization of both the crystalline compound (milled up to 20 h) and the amorphous material is not saturated up to 35 T. This indicates that the magnetic moments are rather randomly distributed in both materials.

The continuous increase of magnetization of CoZr with milling time is as discussed above due to the rearrangement of Co and Zr atoms (atomic disorder) in the B2-lattice by milling. The fact that the starting compound is almost nonmagnetic (the curve 0 h) even at 4.2 K suggests that the as-prepared material is perfectly ordered i.e. both Co and Zr atoms occupy their own sublattices. Upon ball milling the magnetization is increased largely, strongly indicating the generation of anti-site Co atoms. According to the fact that the lattice parameter increases with milling time, it was proposed in Ref. (13) that the type of disorder is anti-site disorder in CoZr. This means that both Co and Zr atoms are able to substitute on each
other’s sublattice. Such an exchange certainly creates anti-site Co atoms and thereby magnetic centres. With increasing milling time the number of magnetic clusters increases. Therefore, the average magnetization increases continuously with milling time. Upon amorphization the magnetization decreases again. This means that the short-range ordered state in the amorphous phase is different from that in the disordered crystalline compound. It is likely that the number of Co–Co nearest neighbours in the amorphous phase is less than in the disordered crystalline compound.

The temperature dependence of the ac magnetic susceptibility $\chi_{ac}$ of CoZr after milling for various periods is shown in Fig. 3 (14). Upon cooling from room temperature to 4.2 K, no anomaly is detected in the starting compound (0 h). This means that the unmilled sample is a paramagnet from room temperature down to 4.2 K. However, upon mechanical milling the material becomes magnetically ordered. After 10 h of milling a pronounced anomaly at about 35 K is observed. This is attributed to a magnetic ordering transition of the disordered crystalline material. We call the corresponding peak ‘peak-I’. The intensity of this transition increases upon further milling. After 20 h of milling another anomaly at about 11 K (peak-II) is visible. After 40 h of milling, the intensity of peak-I decreases somewhat while peak-II grows continuously. After 80 h of milling peak-I is not detectable any more but peak-II grows further. After 160 h of milling, peak-II becomes more pronounced and well-defined. Since the final product after 160 h of milling is amorphous, peak-II must be due to the magnetic ordering transition in the amorphous state. This anomaly already starts after 20 h of milling. This means that then amorphization starts. The amorphous fraction in the sample after 20 h of milling is small so that the shape of the magnetization curve is not significantly influenced. Thus, ac susceptibility measurement provides more accurate information about the structural change of CoZr than X-ray diffraction and magnetization because the magnetic ordering temperature of the disordered crystalline state is quite different from that of the amorphous phase. It was demonstrated in Ref. (14) that both the atomically disordered crystalline and amorphous CoZr are spin glasses with freezing temperatures of 35 and 11 K, respectively.

An increase in high-field magnetization at 4.2 K accompanied by a decrease of the lattice parameter was found in B2 CoGa (15) and B2 CoAl (16) during ball milling. The magnetization of CoGa and CoAl at 4.2 K as a function of milling time is given in Figs. 4 and 5. Again, the increase of magnetization of CoGa and CoAl is attributed to the formation of anti-site Co atoms as explained above.

![Fig. 3 Temperature dependence of the ac susceptibility $\chi_{ac}$ of CoZr after various periods of milling in an external ac field of 3 Oe and a frequency of 109 Hz.](image)

![Fig. 4 Magnetization of CoGa at 4.2 K and 14 T as a function of milling time.](image)

![Fig. 5 Magnetization of CoAl at 4.2 K and 21 T as a function of milling time.](image)
for CoZr. However, in contrast to CoZr, the lattice parameter of both CoGa and CoAl decreases with milling time, indicating a different type of disorder\(^{159\text{a}}\). It was shown\(^{159\text{a}}\) that the type of disorder in CoGa and CoAl is the so-called triple-defect disorder. This special type of disorder also occurs in equilibrium at high temperatures. A triple defect consists of one anti-site Co atom combined with two vacancies on the Co sublattice. The decrease of the lattice parameter can be understood from relaxation around the numerous vacancies.

From the above, it is clear that the high-field magnetization at 4.2 K of B2-structure CoZr, CoGa and CoAl increases largely with milling time due to the introduction of anti-site Co atoms by milling. The measurement of the temperature dependence of the ac susceptibility of CoZr yields a better understanding of the milling process. Non-magnetic CoZr becomes magnetically ordered due to atomic disorder and amorphization. X-ray intensity measurements were not successful to detect the disordering in CoZr. This may be due to the fact that the ball milled material contains many defects which weakens the diffraction intensity and broadens the diffraction peaks so that an accurate evaluation of the change of the relative intensity, i.e. long-range-order parameter is difficult. That in some cases, the information based on superlattice reflections is limited, is also demonstrated by measurements on CoGa and CoAl, where the weak superlattice reflections disappear after long-time milling, although the degree of order remains substantial\(^{159\text{a}}\). In these compounds this effect may have to do with the occurrence of the special type of disorder, viz. triple-defect disorder.

III. B8-Type Compounds with Formula T\(_3\)X\(_2\)

In this section, the compounds Mn\(_2\)Sn\(_2\), Fe\(_3\)Ge\(_2\), Ni\(_2\)Sn\(_2\) and Co\(_2\)Sn\(_2\) with a B8-like structure\(^{177\text{a}}\)–\(^{231\text{a}}\) are considered. Mn\(_2\)Sn\(_2\) and Fe\(_3\)Ge\(_2\) and the high temperature phases (HTPs) of Ni\(_2\)Sn\(_2\) and Co\(_2\)Sn\(_2\) are B8\(_2\) type. This structure is hexagonal and is shown in Fig. 6. The large-filled circles represent the lattice positions occupied by non-transition metal atoms (X) whereas the small open and filled circles represent two different types of interstitial positions that can be occupied by transition metal atoms (T): octahedral (I) and tetrahedral (II) interstices.

The octahedral sites are fully occupied, whereas the tetrahedral sites are only half occupied. The as-prepared low-temperature phases of Ni\(_2\)Sn\(_2\) and Co\(_2\)Sn\(_2\) (LTPs) crystallize in an orthorhombic structure, which exists from room temperature to 873 and 823 K, respectively. The orthorhombic LTPs transform to the hexagonal HTPs by a slight shift in the positions of atoms. The total magnetization of these compounds is expressed by

\[
M = \frac{1}{3} (2 \cdot M_{T1} \pm 1 \cdot M_{T2}),
\]

where \(M_{T1}\) is the spin moment per T atom on I sites and \(M_{T2}\) is the spin moment per T atom on II sites. The factors 2 and 1 account for the occupancies of the respective sites. The plus sign on the right-hand side is for ferromagnetic compounds, whereas the minus sign holds for ferrimagnetic compounds. This means that in ferromagnetic systems the spin moment of transition metal atoms on I sites and II sites are parallel. In contrast, in ferrimagnetic systems the respective spin moments are antiparallel. Furthermore, it is known by neutron diffraction that, in B8 hexagonal Fe–Ge and Mn–Ge and in closely related orthorhombic compounds, the magnetic moment of the transition metal atom on II sites (\(T_{II}\)) is always larger than that of the \(T_{I}\) atoms. The reason for this is that the transition-metal atoms on I sites have different interatomic distances and nearest neighbours than the transition-metal atoms on II sites. Thus, the measurements of changes in magnetic properties after ball milling provide a tool of monitoring changes in occupancies of various sites.

The magnetization at 4.2 K as a function of milling time is shown in Figs. 7–10 for Mn\(_2\)Sn\(_2\), Fe\(_3\)Ge\(_2\), Ni\(_2\)Sn\(_2\) and Co\(_2\)Sn\(_2\). The values of the magnetization were taken from the various high-field magnetization curves at 4.2 K. It is clearly seen that the magnetization of the Fe\(_3\)Ge\(_2\), Ni\(_2\)Sn\(_2\) and Co\(_2\)Sn\(_2\) continuously increases with milling time after various milling periods up to 140 h for Fe\(_3\)Ge\(_2\), up to 32 h for Ni\(_2\)Sn\(_2\) and up to 6 h for Co\(_2\)Sn\(_2\). In con-

![Fig. 6](image_url)

**Fig. 6** The hexagonal B8\(_2\) structure: the large filled circles are the non-transition metal atoms (NT or X); the small open circles are type-I sites; and small filled circles are type-II sites.

![Fig. 7](image_url)

**Fig. 7** Magnetization of Mn\(_2\)Sn\(_2\) at 4.2 K and 21 T as a function of milling time.
In contrast, in Mn$_2$Sn$_2$ the magnetization sharply decreases with increasing milling time when the milling period is shorter than 60 h. A jump-like increase in magnetization is observed in both Ni$_3$Sn$_2$ and Co$_3$Sn$_2$ after 40 and 12 h of milling, respectively. Upon further milling the magnetization tends to become constant in all four compounds. The variation of the magnetization of these compounds is due to a special type of disorder generated by milling\textsuperscript{(17)-(21)} which we called 'redistribution of T atoms over I and II sites'. It means that part of the transition-metal atoms are transferred from I sites to II sites during milling. The magnetization is then determined by the equation

$$M = \frac{2}{3} \left[ (1 - C) \cdot M_{T1} \pm \left( \frac{1}{2} + C \right) \cdot M_{T2} \right],$$

where $C$ represents the fraction of T atoms transferred from I sites to II sites. Fe$_3$Ge$_2$, Ni$_3$Sn$_2$ and Co$_3$Sn$_2$ are ferromagnetic whereas Mn$_3$Sn$_2$ is ferrimagnetic. Thus, the plus sign on the right hand side in eqs. (2) and (3) holds for Fe$_3$Ge$_2$, Ni$_3$Sn$_2$ and Co$_3$Sn$_2$ and the minus sign for Mn$_3$Sn$_2$. If the transition-metal atoms are transferred from I sites to II sites during milling, the fraction $C$ of transition-metal atoms at II sites transferred from I sites continuously increases with milling time, which leads to an increase of the total magnetic moment in Fe$_3$Ge$_2$, Ni$_3$Sn$_2$ and Co$_3$Sn$_2$ and to a decrease of the magnetization in Mn$_3$Sn$_2$. This clearly explains the change of magnetization in the respective compounds. The fact that after milling longer than 140 h for Fe$_3$Ge$_2$, 40 h for Ni$_3$Sn$_2$ and 12 h for Co$_3$Sn$_2$ and 60 h for Mn$_3$Sn$_2$ the value of the magnetization tends to become constant means that C is not increasing during further milling. Apparently a stationary state is then reached. The abrupt increase in magnetization in Ni$_3$Sn$_2$ after 40 h of milling and in Co$_3$Sn$_2$ after 12 h of milling is due to the structural transformation from the orthorhombic LTP to the hexagonal B8-type HTP\textsuperscript{(18,20)-(21)}. So, magnetization measurements in these B8-like compounds result in precise identification of a special type of disorder.

**IV. B8-Type Compounds with Formula T$_2$X**

In contrast to T$_3$X$_2$ compounds, compounds of the B8-like type with formula T$_2$X showed 'normal' anti-site disorder of both components accompanied by an increase of the magnetisation. The compounds studied are low-temperature phase Co$_2$Ge (LTP), high-temperature phase Co$_2$Ge (HTP)\textsuperscript{(20)} and Co$_2$Si\textsuperscript{(23)} A difference between such a T$_2$X compound and T$_3$X$_2$ compounds is the full occupancy of the T sublattices in T$_2$X, so that a redistribution of T atoms over both T sublattices (I and II) is not possible. The magnetic data for T$_2$X are given below.

The magnetization of LTP-Co$_2$Ge at 4.2 K and 21 T for samples milled for various periods is plotted in Fig. 11 as a function of milling time\textsuperscript{(22)}. The filled circle denotes the magnetization of HTP-Co$_2$Ge quenched from 1073 K. From Fig. 11 it is observed that the magnetisation of the LTP (0.11 $\mu_B$/Co atom) is slightly larger
than that of the HTP (0.10 $\mu_B$/Co atom). The magnetization of the LTP increases gradually with increasing milling time when the milling time is shorter than 80 h. After 80 h of milling, it reaches a value of 0.24 $\mu_B$/Co atom. After further milling the magnetization is only slightly dependent on milling time. A ball milling experiment on the HTP was also performed\(^{22}\). It was found that the magnetization also increases upon milling and reaches a final value of about 0.24 $\mu_B$/Co atom\(^{23}\). In Fig. 11, the magnetization of Co$_2$Si at 4.2 K and 21 T is also plotted\(^{23}\). The magnetization first abruptly increases with milling time up to a period of 80 h and then gradually increases upon further milling. It does not become constant even after 629 h of milling.

The continuous increase of magnetization of LTP-Co$_2$Ge, HTP-Co$_2$Ge and Co$_2$Si with milling time is attributed to the generation of anti-site disorder\(^{22,23}\). This means that during mechanical milling Co and Ge or Si atoms exchange position. Such an exchange will lead to a variation of the neighbourhood of a Co atom. It is clear from Fig. 11 that the average magnetic moment of cobalt atoms in ordered LTP- and HTP-Co$_2$Ge, and Co$_2$Si is much less than 1.7 $\mu_B$/Co atom, the value for pure cobalt. The increase in magnetization can then be interpreted as follows: In Co$_2$X, X is a non-magnetic element. This means that only the coordination of the Co atoms determines the formation of the magnetic moment. In the starting compounds, the X atoms surrounding a Co atom hinder the Co-Co interaction, which limits the formation of a large magnetic moment. During mechanical milling, due to the exchange of Co and X atoms, the neighborhood of a Co atom will change. In this way clustering is favoured with more and more Co atoms surrounding a Co atom. Such a Co-rich cluster will bear a larger magnetic moment because of an increasing probability of Co-Co exchange interactions. The number of the Co-rich clusters will gradually increase with increasing milling time. This will lead to an increase of the average magnetization. Therefore, it is observed that the magnetization of Co$_2$Ge and Co$_2$Si continuously increases with milling time. So, the continuous increase of the magnetization gives evidence that by mechanical milling anti-site disorder is generated in Co$_2$Ge and Co$_2$Si.

The measurement of the a.c. susceptibility on ball milled Co$_2$Ge gives more insight into the structural change of Co$_2$Ge upon milling. The temperature dependence of the a.c. susceptibility of both the LTP and HTP after various periods of milling is given in Figs. 12 and 13, respectively\(^{22}\). From Fig. 12 it is clear that in the early stage of milling (up to 60 h), the Curie temperature of ferromagnetic LTP-Co$_2$Ge increases with milling time due to the increased magnetization. Upon amorphization (between 60 and 180 h), an anomaly corresponding to the magnetic transition of the amorphous phase is observed. Upon the completion of amorphization this anomaly becomes well-defined (180 h). Upon further milling this transition becomes sharper and sharper, indicating homogenization of the amorphous material. In contrast, hardly any change is observed in X-ray diffraction\(^{22}\). Therefore, it is concluded that the measurement of magnetic properties gives more insight than X-ray diffraction during the intermediate stage of milling. Amorphous Co$_2$Ge turns out to be a novel spin glass\(^{24}\). Typical results are also presented in Section VII. Ball milling of HTP-Co$_2$Ge has the same result as of the LTP. From Fig. 13 it is clear that in the early stage of milling (up to 5.7 h), the Curie temperature of ferromagnetic HTP-Co$_2$Ge increases with milling time. Upon amorphization the material becomes also a spin glass\(^{25}\).

### V. L1$_2$-Structure Compounds T$_1$X

Magnetic measurements were also used to study the behaviour of L1$_2$ compounds upon milling. The studied compounds are Ni$_2$Si, Ni$_2$Al and Fe$_2$Ge\(^ {25-27}\). Among them, the influence of milling on the magnetization of Ni$_2$Al is particularly pronounced. Thus, one can learn more about the structural change of Ni$_2$Al upon ball milling from magnetic data than from X-ray diffraction. In Fig. 14, the high-field magnetization curves at 4.2 K up to 21 T of Ni$_2$Al milled up to 60 h are displayed. The magnetization at 21 T is plotted in Fig. 15 as a function of milling time. It is clear that upon ball milling both the magnetic susceptibility and the magnetization of Ni$_2$Al at 21 T change drastically. The magnetization decreases almost linearly with increasing milling time (Fig. 15) up to about 5 h of milling. Upon longer milling, it decreases further till 40 h of milling, where a constant value is reached. No clear change is observed upon continued milling. It was demonstrated by Arrott plots and measurement of the temperature dependence of the a.c. susceptibility that ferromagnetic Ni$_2$Al in fact becomes paramagnetic after long periods of milling\(^ {27}\). The magnetization of ball-milled Ni$_2$Si at 4.2 K and 14 T taken from the respective magnetization curves is plotted in Fig. 16 as a function of milling time. Milling for 4 h results in a rapid decrease of the magnetization. Upon further milling, the
magnetization is hardly affected.

High-field magnetization measurements at 4.2 K up to 14 T were also performed on various Fe$_3$Ge samples. Typical results are shown in Fig. 17. The magnetization increases after 2 h of milling where complete disorder is reached in the L1$_2$ structure and where a small fraction of b.c.c. solid solution is obtained. However, after 5 h of milling the magnetization is again lower. This is due to a further phase transformation from f.c.c. to b.c.c., because the magnetization of the b.c.c. solution is lower than of the f.c.c. sample as seen in Fig. 17 for the sample milled for 130 h, where a single b.c.c. phase is obtained. The increase of the high-field magnetization at 4.2 K in L1$_2$-Fe$_3$Ge is due to the introduction of anti-site disorder in the L1$_2$-f.c.c. lattice, leading to an increase of the number of Fe-Fe nearest neighbours from 8 in the ordered L1$_2$ to 9 on the average in disordered L1$_2$. It is interesting to note that the phase transformation from disordered L1$_2$,f.c.c. to the disordered b.c.c. is accompanied by a decrease of magnetization at 4.2 K. This is due
Fig. 13  Temperature dependence of the real part of the a.c. magnetic susceptibility $\chi'$ of HTP-Co$_2$Ge after various periods of milling in an external a.c. field of 0.6 Oe and a frequency of 109 Hz.

Fig. 14  High-field magnetization curves at 4.2 K of Ni$_2$Al after various periods of milling.

to the fact that the average number of Fe–Fe nearest neighbours in the b.c.c. lattice is on the average 6 which is less than in the f.c.c. lattice. Apparently, the number of nearest-Fe neighbours determines the magnetization. Let us inspect the value of the magnetization at 14 T, the highest field used. $M$ increases in the early stage, when the number of Fe-nearest neighbours increases from 8 to 9. Subsequently, it decreases in the period from 2 to 130 h of milling, when the number of Fe-nearest neighbours decreases from 9 to 6. Can magnetization be that simple, that the number of nearest neighbours is proportional to

Fig. 15  Magnetization of Ni$_2$Al at 4.2 K and 21 T as a function of milling time.

Fig. 16  Magnetization of Ni$_2$Si at 4.2 K and 14 T as a function of milling time.

Fig. 17  High-field magnetization curves at 4.2 K of Fe$_2$Ge after various periods of milling.
the magnetization, i.e.

\[
\Delta M(L_1-f.c.c.) = M(8 \text{ Fe neighbours}) - M(9 \text{ Fe neighbours}) \\
= 1/2 \times \Delta M(b.c.c. - L_1) \\
= 1/2 \times (M(6 \text{ Fe neighbours}) \\
- M(8 \text{ Fe neighbours})).
\]

For the magnetization at 14 T, eq. (4) is fulfilled almost exactly!

Why the magnetization of both Ni$_3$Si and Ni$_3$Al decreases upon anti-site disordering is not clear yet. It is remarkable that both Ni$_3$Si and Ni$_3$Al behave in the same manner upon disordering. The number of Ni-Ni nearest neighbours in ordered L1$_2$ is 8 whereas in disordered f.c.c. it is 9 on the average. Apparently, the picture of the local environment which was successfully used for Co-based compounds in previous sections and for Fe$_2$Ge does not work for Ni-based L1$_2$ compounds. The difference in magnetic behaviour upon disordering between Co and Fe compounds on the one hand and Ni compounds on the other hand has certainly to do with the difference in magnetic character of Co and Fe on the one hand and Ni on the other.

If we compare magnetic data of Ni$_3$Al with X-ray diffraction results, one can see that magnetic measurements give more insight into the structural change of Ni$_3$Al. The long-range-order (LRO) parameter S of Ni$_3$Al derived from the X-ray superlattice reflections by using eq. (1) is given in Fig. 18 and is found to decrease linearly and reaches a zero value after about 6 h of milling. This may mean that the material reaches a completely disordered state after 6 h of milling and that a phase transformation to the f.c.c. solid solution is realized. But, by careful inspection of both Figs. 15 and 18 it is found that, when the S value becomes zero after about 6 h of milling, the magnetization still continuously decreases upon further milling. The magnetization starts to become constant after 20 h of milling, well after the disappearance of the superlattice reflections (S = 0). A similar tendency is observed in the change of the lattice parameter, i.e. after 20 h of milling it starts to become constant. These observations strongly suggest that structural changes still take place even after the disappearance of LRO. It could be that existing short-range-order (SRO) is destroyed or that the measured intensities of the superlattice reflections are not completely decisive for the evaluation of atomic order, or that the material decomposes into two phases with different composition (f.c.c. solid solution and some amorphous phase). Of course, there might be another possibility for the decrease of magnetization between 6 and 40 h of milling. That is the reduction of the crystallite size, whereby a substantial fraction of atoms could reside in grain boundaries. However, this seems not probable because the average crystallite size tends to become constant already after about 5 h of milling with a final size of about 25 nm. This value is much larger than the limit for the reduction of magnetization due to grain-boundary atoms, which is usually 4–6 nm. Therefore nanocrystallinity does not seem to explain the decreasing magnetization. As discussed for CoZr in Section II, an accurate measurement of the change of the relative intensity i.e. the LRO parameter is difficult because ball-milled materials contain many defects which make the diffraction intensity very low and the diffraction peaks rather broad. The change of the magnetization reflects the change of the nearest-neighbour configuration of the magnetic element (here Ni). Therefore, the magnetization is more sensitive to structural changes than the X-ray intensities. The information obtained from X-ray diffraction is limited, in particular during the intermediate stage of milling.

VI. Other Compounds

Magnetic measurements were also performed on a few other compounds namely CoV(28) and FeCr(29) sigma phases and GdAl$_2$ Laves phase(30)(31). As an example, the magnetization of CoV at 4.2 K and 21 T derived from various magnetization curves is plotted in Fig. 19 as a function of milling time. It is clear that the magnetization of CoV increases gradually with increasing milling time up to a period of 20 h. After 40 h of milling a large increase in magnetization is observed. Upon further milling the magnetization increases further. After 80 h of milling it tends to become constant. The increase of magnetization was well-explained according to the environment model as used above for Co- and Fe-based compounds(28). An increase of the magnetization was also found in FeCr(29) sigma phase in the early stage of milling.

High-field magnetization measurement of the ferromagnetic Laves phase GdAl$_2$ showed that both the magnetization and in particular the magnetic susceptibility change drastically upon milling. The high-field susceptibility increases strongly with increasing milling time. For the samples milled for long time, the magnetization does not saturate in a field of 21 or even 35 T(31). This indicates that upon mechanical milling the Gd moments in GdAl$_2$
tend to be randomly distributed as a significant consequence of atomic (chemical) disorder, i.e. the atoms are transferred to the 'wrong' sublattice. Simultaneously, the magnetization at 4.2 K decreases with milling time\(^{39}\). The temperature dependence of the a.c. susceptibility \(\chi_{ac}\) of GdAl\(_3\) after various periods of milling is given in Fig. 20\(^{39,30}\). 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. 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 completely disappeared. 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 new magnetic phase. Both the peak temperature (see Fig. 20) and the intensity increase with milling time, indicating the homogenization and the increase of the amount of this new magnetic phase. After 600 h of milling, the material has completely transformed to this new magnetic phase. The transition temperature becomes constant at value of 65 K after milling for 1000 h or longer. This new magnetic phase turns out to be a new spin-glass phase and not a ferromagnet\(^{39}\). The evidence for this will also be given in Section VII. The above observation is consistent with X-ray diffraction results\(^{31}\) and gives more insight in the structural changes during the intermediate stage of milling. On the basis of magnetic data a new type of disorder was proposed namely 'quadruple-defect disorder'\(^{31}\).

Fig. 19 Magnetization of CoV at 4.2 K and 21 T as a function of milling time.

Fig. 20 Temperature dependence of the a.c. susceptibility \(\chi_{ac}\) of GdAl\(_3\) in an external a.c. field of 1.2 Oe and a frequency of 109 Hz after various periods of milling.

VII. Novel Spin Glasses by Mechanical Milling

The first spin glass discovered in ball-milled materials is the binary amorphous Co\(_2\)Ge alloy\(^{30}\). Amorphous Co\(_2\)Ge was obtained by mechanical milling of the Co\(_2\)Ge crystalline compound. The amorphous state cannot be obtained by melt-spinning. The crystalline Co\(_2\)Ge com-
pound turned out to be ferromagnetic at the lower temperature, whereas amorphous Co$_2$Ge takes the spin-glass state at 220 K. Figure 21 gives the temperature dependence of the a.c. magnetic susceptibility of amorphous Co$_2$Ge in different applied fields at a frequency of 109 Hz. A sharp asymmetric cusp at 41 K is observed when the field is low. This cusp looses its sharpness and becomes a rounded maximum by an increase of the external field. Both the peak intensity and the peak temperature decrease with increasing field. These results are further confirmed by the static susceptibility measurements and the observation of thermal hysteresis in low magnetic fields below freezing temperature $T_I$.

Atomically disordered crystalline GdAl$_3$ is the second novel spin-glass material obtained by mechanical milling. The $M/B$ vs $T$ curves of disordered crystalline GdAl$_3$ (milled for 1000 h) in different external d.c.-fields are given in Fig. 22 after zero-field cooling (ZFC, open symbols) and field cooling (FC, filled circles). After cooling the sample to 4.2 K in zero field and in an external field the measurement was successively made during heating. The $M/B$ value gives the initial dc-susceptibility, $\chi_{dc}$, when the applied fields are small so that the magnetization is proportional to susceptibility. Now let us inspect the ZFC curves (open symbols). Upon application of a field of 40 Oe a sharp maximum is observed like in the a.c. susceptibility. This maximum becomes a rounded transition and shifts to lower temperature with increasing field. The value of $M/B$ also decreases with increasing field. A similar behaviour is also observed in the a.c. susceptibility vs temperature curve.

The two $M/B$ vs $T$ curves in Fig. 22 measured in a field of 220 Oe (circles) after ZFC and FC illustrate the irreversibility in disordered GdAl$_3$ at temperatures below $T_I$, a characteristic feature of a spin glass. The features at and below $T_I$ are remarkable. 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 $T_I$, where the two curves coincide. Moreover, the ZCF magnetization is irreversible. So, the d.c. field, when applied below $T_I$, creates a metastable and irreversible state in disordered GdAl$_3$.

These phenomena are very similar to those reported for the prototype spin glasses e.g. FeAu and MnCu$_2$. Thus, the magnetic properties of amorphous Co$_2$Ge and atomically disordered crystalline GdAl$_3$ are characteristic of spin glasses. As shown above, both the originally ordered Co$_2$Ge and GdAl$_3$ are ferromagnets at lower temperature. After milling both materials become spin glasses as a consequence of disorder on an atomic level. Thus the magnetic properties of the metastable phases obtained by milling are markedly different from their stable forms. Therefore, mechanical milling is a novel and subtle technique to synthesize various new metastable materials such as novel spin glasses.

**VIII. Conclusions**

Mechanical milling of intermetallic compounds usually has a significant influence on magnetic properties as a consequence of atomic disorder and/or disorder-induced
phase transformation. On the one hand, the measurement of magnetic properties forms an important tool for monitoring the structural changes of intermetallic compounds during milling. In particular, in case there is no significant change in X-ray diffraction patterns and DSC traces in the intermediate stage of milling, it can provide detailed and precise information about the structural change of the compounds during milling. This leads to a much better understanding of the mechanisms governing ball-milling-induced phase transformations in intermetallic compounds. On the other hand, milling may induce in the material unusual and interesting magnetic properties. Thus, high-energy ball milling is a very promising non-equilibrium processing technique and can be generally used to synthesize various types of new materials. This is illustrated by the discovery of a number of novel spin glasses, which proves that mechanical milling is a subtle technique to synthesize such a subtle state as the spin glass state. On the one hand, ball milling is simple, inexpensive, and easily controllable. On the other hand, ball milling not only can synthesize materials which can also be obtained by traditional rapid solidification techniques, but also, even more important, can synthesize materials which cannot be produced by other methods, e.g. immiscible systems. In this way ball milling turns out to be a unique technique.

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REFERENCES