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Evidence for atomic disorder in $B8$-structure Mn-Sn by mechanical milling

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Mechanical milling of ferrimagnetic $B8$-structure $Mn_{1.5}Sn$ results in a decrease of the magnetization at 4.2 K in a field of 21 T. This is in contrast to a number of other ferromagnetic $B8$-structure compounds, where the magnetization increases. The explanation is given in terms of a redistribution of transition-metal atoms over two different types of transition-metal sites. The Curie temperature (T_C) of the compound also decreases. The unit-cell volume increases with milling time, which provides additional evidence for the particular type of atomic disorder. The material remains in its original crystal structure even after prolonged periods of ball milling.

By mechanical milling an ordered intermetallic compound can transform to the amorphous state[1,2] or to a disordered solid solution of the one component in the other component.[3] In recent investigations,[4,5] we discovered a different type of phase transformation: the transformation from an orthorhombic low-temperature phase (LTP) to a hexagonal ($B8$-structure) high-temperature phase (HTP). This was found for the intermetallic compounds Ni_3Sn_2 and Co_3Sn_2. Here we are dealing with the transformation from one complex crystal structure to a somewhat simpler but still complex structure. During ball milling the magnetization of both compounds turned out to increase sharply with increasing milling time. To suggest an explanation for this effect it is useful to inspect the crystal structure of these compounds more closely. In the $B8$ structure there are two interstices that can be occupied by the transition-metal atoms: octahedral (I) and tetrahedral (II) interstices. In the HTP of Ni_3Sn_2 and Co_3Sn_2 all of the I sites and only half of the II sites are occupied in order to obtain the correct composition. In fact the LTP is very similar to the HTP, only the atoms are shifted somewhat from their positions to form an orthorhombic structure. It is interesting to note that the magnetic moment of the transition-metal atoms on I sites is lower than on II sites. Considering the crystal structure of the compounds and the difference in magnetic moment of transition-metal atoms in both interstice positions, a plausible explanation seemed to be that during ball milling transition-metal atoms are transferred from I sites to II sites. In other words, by ball milling the "interstitial" transition-metal atoms would be redistributed over the octahedral (I) and tetrahedral (II) sites. By prolonged milling the material transformed from the LTP structure to the HTP structure. After transformation, the magnetization of the HTP did not increase any more upon further milling. The magnetization of the HTP, obtained by ball milling was found to be considerably higher than that of quenched HTP. This was explained by assuming that the transition-metal atoms that were redistributed over the two different interstices during ball milling of the LTP remain there after the diffusionless phase transformation. If this explanation is correct, the mechanical milling process would be a unique technique to induce a metastable, disordered state of a special type in these B8-type compounds.

In order to confirm this type of atomic disorder and to assess that no other effects were responsible for the increase of the magnetization we devised a crucial experiment. We studied the behavior of $B8$-structure Mn-Sn during mechanical milling. The reason why we selected the manganese-tin compound is as follows. Judging by the decrease of magnetization with increasing manganese concentration[6,7] $B8$-structure Mn-Sn is not ferromagnetic as are Co_3Sn_2 and Ni_3Sn_2,[4,8] but is *ferrimagnetic* below the Curie temperature. This means that the spin moments of the manganese atoms on I sites are not parallel, but in contrast *antiparallel* to those on II sites. The total magnetic moment per Mn atom of $Mn_{1.5}Sn$ is then described by $M=(1M_{\mathrm{MnI}}-0.5M_{\mathrm{MnII}})/1.5$, where M_{MnI} is the spin moment per Mn atom on I sites and M_{MnII} is the spin moment per Mn atom on II sites. In contrast, for the iron, cobalt, and nickel compounds the right-hand side of this equation contains a plus sign instead of a minus sign. The idea is now that if redistribution of transition-metal atoms over I and II interstices really takes place then the total magnetization of $Mn_{1.5}Sn$ would decrease by ball milling, in contrast to the iron, cobalt, or nickel compounds, where it increases. Among the transition-metal–tin systems, the homogeneous range of the $B8$ structure in the Mn-Sn system is rather wide.[9-11] This structure is hexagonal as is the HTP of Ni_3Sn_2 and Co_3Sn_2. In order to make the results comparable, we chose the same composition as in the Ni-Sn and Co-Sn systems, so $Mn_{1.5}Sn$.

The starting compound $Mn_{1.5}Sn$ was prepared by arc melting of weighed amounts of pure manganese and tin in a purified argon atmosphere. Then the sample was sealed in a quartz tube under argon atmosphere and annealed at 600 °C for 10 days. The x-ray diffraction pattern of the annealed sample shows a single phase with the $B8$-hexagonal structure (space group $P6_3/mmc$). The ball milling was carried out in a hardened steel vial and, in order to prevent reactions with oxygen or nitrogen, in a vacuum of about 10^{-6} Torr. The starting amount of material was three grams. Powders for magnetic measurements were taken from the samples milled for different periods and after that the powder was used for x-ray-diffraction. X-ray-diffraction patterns were taken at room temperature by means of a Philips diffractometer with vertical goniometer using Cu$K\alpha$ radiation. For an accurate measurement of the lattice parameters the powder sample was mounted on the sample holder with

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silicon as a standard. The temperature dependence of the magnetization was measured from room temperature to liquid-helium temperature in a self-constructed magnetometer. The high-field magnetization measurements at 4.2 K were performed in the Amsterdam High Field Installation[12] in which magnetic fields up to 40 T can be generated in a semi-continuous way. A stepwise field profile up to 21 T was used. The sensitivity of this magnetometer is about 10^{-5} A m^2.

X-ray-diffraction patterns of $Mn_{1.5}Sn$ after various periods of milling are shown in Fig. 1. The pattern of the as-prepared material (0 h) is characteristic of the *B*8-hexagonal structure (space group $P6_3/mmc$) with some superlattice reflections (indicated by filled circles in Fig. 1), which can be indexed using $a_s \approx a$ and $c_s \approx 3c$, where a and c are the lattice parameters of the *B*8 structure. These superlattice reflections result from the long-range ordered distribution of the holes on the II sites of the *B*8 structure of Mn-Sn. Some of the peaks, the behavior of which will be discussed below, are indexed explicitly in Fig. 1. It is clearly visible that the intensity of all the superlattice reflections and of the [100], [203] reflections decreases with increasing milling time and that these reflections eventually disappear. The "fundamental" Bragg peaks of the *B*8-structure Mn-Sn become broader upon milling. In fact, after 10 h of milling most peaks originating from the superlattice reflections have disappeared, but the fundamental reflections remain. After 30 h of milling, all the peaks from superlattice reflections except for the [320] reflection and the peaks from the [100] and the [203] reflections disappeared. Meanwhile the [102] and [110] peaks, [212] and [300] peaks cannot be distinguished any more. Apparently, after 60 h of milling, x-ray-diffraction patterns do not change any further. After prolonged periods of milling the material does not go to the amorphous state. The broadening of the peaks is ascribed to development of stresses and refinement of crystallite sizes. Based on the width of Bragg peaks, the crystallite size can be estimated after correction for internal strain broadening. The crystallite size of the sample after 5 h of milling is about 90 nm. The crystallite size is estimated as 6.0 nm for the sample after 80 h of milling. This means that a nanocrystalline structure is also formed during the late stage of milling.

The lattice parameters a and c, derived from the x-ray-diffraction patterns of $Mn_{1.5}Sn$ after various milling periods as well as the unit-cell volume are shown in Fig. 2. It can be seen that the length of the a axis increases with increasing milling time, whereas the c axis decreases gradually upon milling. After 40 h of milling, both a axis and c axis tend to become constant. The unit-cell volume of $Mn_{1.5}Sn$ increases with increasing milling time and becomes nearly constant after 40 h of milling. The relative increase (about 1.3%) is almost the same as in Ni_3Sn_2 (about 1%).

The magnetization at 4.2 K of $Mn_{1.5}Sn$ after milling at 21 T taken from the various magnetization curves as a function of milling time is shown in Fig. 3. For compar-

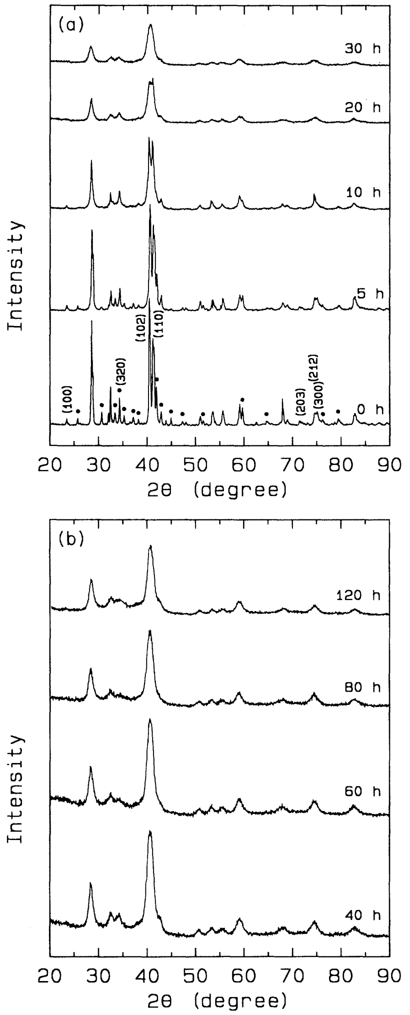

FIG. 1. X-ray-diffraction patterns of $Mn_{1.5}Sn$ after various periods of milling.

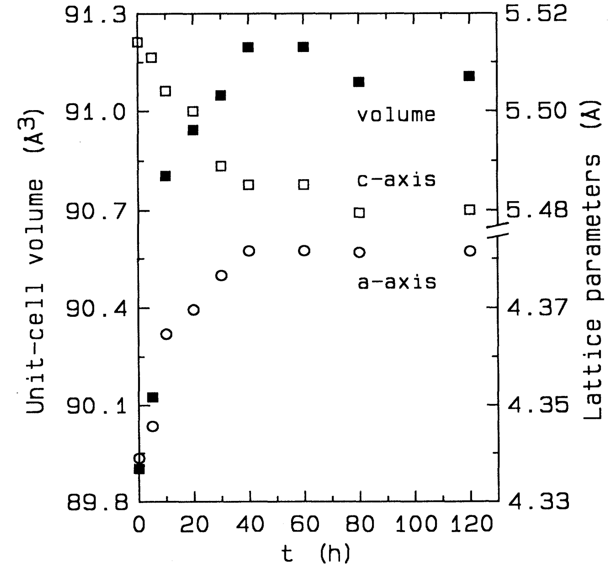

FIG. 2. Lattice parameters (open markers and the right-hand-side scale) and unit-cell volume (filled squares and the left-hand-side scale) of $Mn_{1.5}Sn$ as a function of milling time.

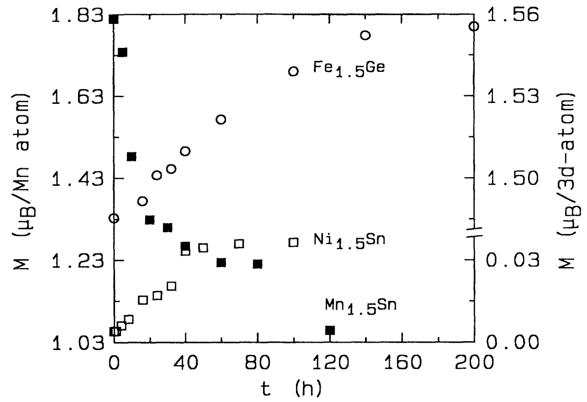

FIG. 3. Magnetization at 4.2 K of $Mn_{1.5}Sn$ (filled squares and the left-hand-side scale), $Fe_{1.5}Ge$ (open circles) as well as $Ni_{1.5}Sn$ (open squares and the right-hand-side scale) at 21 T as a function of milling time.

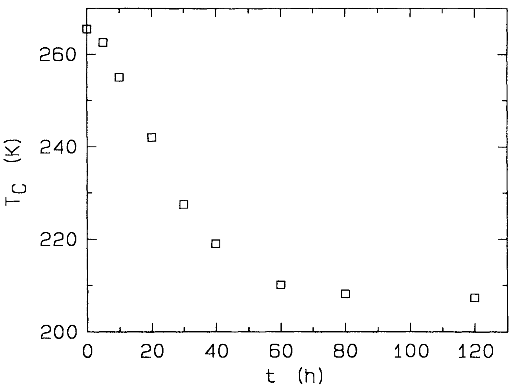

FIG. 5. Curie temperature (T_C) of $Mn_{1.5}Sn$ as a function of milling time.

ison, the magnetizations at 4.2 K of the ferromagnetic $Fe_{1.5}Ge$ and $Ni_{1.5}Sn$ at 21 T as function of milling time are also given in Fig. 3. The crystal structure of $Fe_{1.5}Ge$ is exactly the same as that of $Mn_{1.5}Sn$, while the structure of $Ni_{1.5}Sn$ is similar to that of $Mn_{1.5}Sn$. It is clearly seen that the magnetization sharply decreases with increasing milling time for milling periods shorter than 60 h. Upon further milling the magnetization decreases gradually and tends to become constant. After 120 h of milling, the magnetization drops down again. In $Fe_{1.5}Ge$ and $Ni_{1.5}Sn$, however, the magnetization increases gradually with milling time in the early stage of milling. After long-time milling it tends to become constant in both $Fe_{1.5}Ge$ and $Ni_{1.5}Sn$.

The typical temperature dependence of the magnetization in an external field of 0.5 T of $Mn_{1.5}Sn$ after various periods of milling is shown in Fig. 4. It can be seen that for all samples there is a magnetic order transition with characteristics of a ferriparamagnetic transition. The Curie temperature T_C derived from the corresponding M^2-T curves is plotted in Fig. 5 as a function of milling time. It is clearly seen that the T_C value decreases linearly with increasing milling time up to 60 h of milling and it tends to become constant upon further milling.

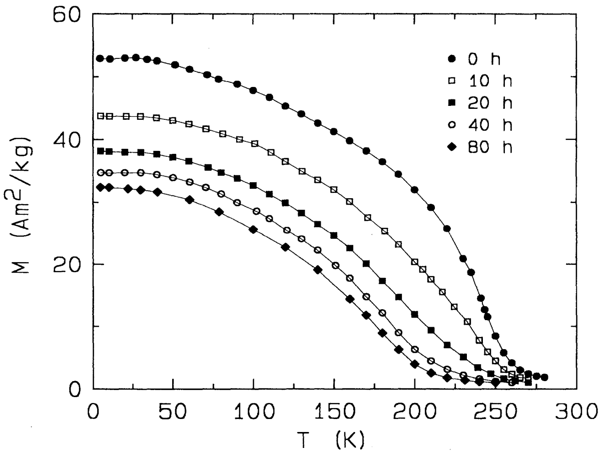

FIG. 4. Typical temperature dependence of the magnetization in an external field of 0.5 T of $Mn_{1.5}Sn$ after various periods of milling.

Let us now discuss the variation of the magnetization. In the $B8$-hexagonal structure $Mn_{1.5}Sn$, the magnetic moment of Mn atoms on I sites can be different from that of Mn atoms on II sites, since they have different interatomic distances and nearest neighbors. It was found in similar compounds (see, for example, Ref. 13 for $B8$-structure Fe-Ge and Mn-Ge) by neutron diffraction that the magnetic moment of the transition-metal atom on II sites (T_{II}) is always larger than the moment of the T_{I} atom. In the equilibrium state the I positions are fully occupied by Mn, the II positions are only half filled. During ball milling, it is likely that the Mn atoms make ballistic jumps from I sites to II sites. The fraction of the Mn atoms at II sites jumping from I sites then increases with the milling time, which leads to the sharp decrease of total magnetic moment due to $M=[(1-x)M_{\mathrm{MnI}}-(0.5+x)\,\mathrm{Mn}_{\mathrm{MnII}}]/1.5$, where x is the fraction of the Mn atoms jumping from I sites to II sites. In this equation the minus sign is of major importance (ferrimagnet) because it explains the decrease in the magnetization. The decrease of the magnetization fully confirms the special type of disorder generated by ball milling. The fact that after 60 h of milling the magnetization tends to become constant indicates that the x value cannot be increased any more upon further milling. This means that by further milling no more manganese atoms can be driven from I sites to II sites. However, the material is still refined upon further milling.[8] The drop of the magnetization after 120 h of milling may be due to this refinement of crystallites. In contrast to $Mn_{1.5}Sn$, in ferromagnetic $Fe_{1.5}Ge$ and $Ni_{1.5}Sn$, the above equation has a plus sign. Due to the transfer of transition-metal atoms from I to II sites, it is expected that the total magnetization increases with increasing milling time. This is experimentally observed indeed (see Fig. 3).

By inspecting Fig. 2, we find that in the early stage of milling the length of the a axis increases, whereas the c axis decreases with increasing milling time and that the unit-cell volume increases. In the starting compound the I sites are fully occupied by Mn atoms, whereas II sites are only half occupied. The volume of octahedral interstices (I) is larger than that of tetrahedral interstices (II). If the Mn atoms on I sites can really jump to II sites driven by the mechanical energy supplied by ball milling, a volume explansion is expected. The reason for this is as follows. When an atom jumps from a I site to a II site, a I site is emptied, whereas a II site is filled. Stress relaxation around the vacant I site will lead to a decrease of the unit-cell volume (ΔV_0). However, filling of a II site will probably lead to a stronger increase of the unit-cell volume (ΔV_i). This means an increase in unit-cell volume, since $\Delta V = \Delta V_i - \Delta V_0$ is positive. This is experimentally observed. This gives another evidence that the Mn atoms are really displaced from I sites to II sites during milling.

The decrease of T_C value of $\mathrm{Mn}_{1.5}\mathrm{Sn}$ during mechanical milling is mainly due to the atomic displacements. This can be explained as follows: For the transition-metal–tin intermetallics with $B8$ structure it was pointed out that, among the exchange interactions of two manganese atoms on I sites J_{11}, on a I site and a II site J_{12}, and on two II sites J_{22}, the exchange interaction J_{12} is predominant, and that the Curie temperature is determined by this quantity.[7] In the equilibrium state the I positions are fully occupied by Mn atoms (Mn_{I}), whereas the II positions are only half filled by Mn atoms ($\mathrm{Mn}_{\mathrm{II}}$). Judged by the superlattice reflections [see Fig. 1(a) the peaks indicated by filled circles], the $\mathrm{Mn}_{\mathrm{II}}$ atoms and holes are in a long-range-ordered way distributed over the II positions. The superexchange interaction between Mn atoms on I sites and on II sites may play an important role in determining the Curie temperature of $\mathrm{Mn}_{1.5}\mathrm{Sn}$. During ball milling, the Mn atoms jump from I sites to II sites. This will lead to a redistribution of $\mathrm{Mn}_{\mathrm{II}}$ atoms and holes over the II positions and to a redistribution of Mn atoms over I and II positions. The redistribution of $\mathrm{Mn}_{\mathrm{II}}$ atoms and holes over the II positions may lead to a decrease of the long-range-ordered arrangement of $\mathrm{Mn}_{\mathrm{II}}$ atoms and holes, and thus lead to a decrease of the superexchange interaction between Mn_{I} and $\mathrm{Mn}_{\mathrm{II}}$. Then T_C may be decreased by the decrease of superexchange interaction. As shown in Fig. 1, in the early stage of milling, the x-ray-diffraction intensity of the superlattice reflections decreases sharply with increasing milling time, while the T_C value also decreases sharply. After the disappearance of all the superlattice reflections except for the [320] reflection, the material becomes short-range ordered. Then, the gradual decrease of T_C upon further milling can be analyzed by a mean-field approximation. The Curie temperature is related to the exchange interaction constant J_{MnMn} and the magnetization via the expression (see Ref. 8 for details):

$$T_C = 4J_{\mathrm{MnMn}}(1+x-2x^2)S_{\mathrm{Mn}}(S_{\mathrm{Mn}}+1)/5k_B \ , \qquad (1)$$

$$S_{\mathrm{Mn}} = \{[1+4\sqrt{S_{\mathrm{I}}S_{\mathrm{II}}(S_{\mathrm{I}}+1)(S_{\mathrm{II}}+1)}]^{1/2}-1\}/2 \ , \qquad (2)$$

where S_i (i=I,II) is the so-called pseudospin for the $3d$ electrons via the observed atomic $3d$ magnetic moment $M_i = g_{\mathrm{Mn}}\mu_B\, S_i$ (i=I,II). g_{Mn} is the Landé factor, μ_B the Bohr magneton; k_B is the Boltzmann constant and x ($0 \le x \le 0.5$) the fraction of Mn atoms going from I sites to II sites. Due to the atomic displacements from I sites to II sites upon further milling, the x value is increasing. This will lead to an increase of the term $(1+x-2x^2)$ in Eq. (1) due to $0 \le x \le 0.5$. If we assume the value of J_{MnMn} would not change any more upon milling, there would be an increase in T_C value. However, it was experimentally observed that the T_C value of $\mathrm{Mn}_{1.5}\mathrm{Sn}$ still decreases gradually upon further milling, which means that, in fact, the exchange interaction constant J_{MnMn} is decreasing with increasing milling time in the later stage of milling. This is in good agreement with the results in $\mathrm{Ni}_3\mathrm{Sn}_2$.

In summary we have observed that the magnetization of $\mathrm{Mn}_{1.5}\mathrm{Sn}$ decreases sharply with increasing milling time when the milling period is shorter than about 60 h. The magnetization tends to become constant upon further milling. After 120 h of milling, the magnetization drops down. The sharp decrease of the magnetization at 4.2 K is due to the very special, so far unknown type of atomic disorder, which we called "redistribution of 'interstitials.'" This means a transfer of transition-metal atoms from I sites to II sites. This redistribution gave an increase in magnetization in ferromagnetic $\mathrm{Fe}_{1.5}\mathrm{Ge}$, $\mathrm{Ni}_{1.5}\mathrm{Sn}$, and $\mathrm{Co}_{1.5}\mathrm{Sn}$, whereas it causes a decrease in magnetization in ferrimagnetic $\mathrm{Mn}_{1.5}\mathrm{Sn}$, completely as expected. Values of the Curie temperature of $\mathrm{Mn}_{1.5}\mathrm{Sn}$ decrease with increasing milling time. This is due to the decrease of the Mn-Mn coupling strength by the redistribution of manganese atoms during ball milling. The continuous increase of the unit-cell volume gives another evidence for the particular type of atomic disorder. Apart from a confirmation of the special disordering process by ball milling, from the present experiment it should also be clear how useful magnetic measurements may be for monitoring structural changes in materials. The present investigation also provides important information for understanding the mechanism of mechanical milling process of intermetallic compounds.

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