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Mechanical attrition and magnetic properties of CsCl-structure Co-Ga

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Structural changes in stoichiometric CoGa during mechanical attrition in a high-energy ball mill were monitored by measurements of magnetic properties and lattice parameter. The high-field magnetization increases, whereas the lattice parameter decreases as a function of milling time. For long milling times, values of both parameters saturate. The results are interpreted by the generation of atomic triple-defect disorder, also characteristic of this compound in equilibrium at high temperatures: antisite Co atoms in combination with vacancies on the Co sublattice in a ratio 1:2. By comparison to the magnetic properties of Co_xGa_{100-x} compounds with excess Co, the fractions of antisite Co atoms and vacancies are derived. On the basis of these values, the decrease of the lattice parameter can be calculated and compared to the actual measurement. The good agreement proves that, by the apparently crude technique of mechanical attrition, well-defined nonequilbrium states in intermetallic compounds can be generated.

I. INTRODUCTION

In 1983, Koch *et al.*[1] reported the amorphization of a Ni-Nb alloy during mechanical alloying of elemental powders in a high-energy ball mill. Since then, this process has attracted much attention and a substantial number of alloy systems were found to amorphize in a ball mill.[2] In this process, the gain of free energy resulting from the mixing of the elements is assumed to be the driving force for the reaction, while the formation of intermetallic compounds with a still lower free energy is suppressed.[3] However, two years before the discovery by Koch *et al.*, Yermakov *et al.*[4] demonstrated that, even starting from prealloyed material, amorphization may occur during ball milling. In contrast to mechanical alloying, in this case there is an increase in energy when the material transforms from the crystalline to the amorphous state. Apparently, the reaction is driven by the storage of mechanical energy in the material during ball milling. A similar reaction may take place in compounds under irradiation: when an intermetallic compound is irradiated by heavy ions, amorphization may result. In this process, atomic (chemical) disorder was demonstrated to precede the amorphization.[5] In analogy to irradiation, the occurrence of atomic disordering seems also plausible in the early stage of mechanical attrition. This disorder may eventually lead to amorphization. The storage of energy in the form of atomic disorder was investigated in a number of theoretical studies,[6-9] while experimental evidence was given on the basis of differential scanning calorimetry (DSC) and lattice parameter measurements.[10] In a recent paper[11] we demonstrated that chemical disorder occurs in Nb_3Sn during the early stage of ball milling. The disordering in this material was monitored by a decrease of the superconducting transition temperature and an increase of the lattice parameter as a function of milling time. The observed behavior turned out to be similar to that of *A*15 compounds during neutron irradiation or after quenching from high temperatures. Since the latter treatments are known to induce antisite disorder, it was concluded that also during mechanical attrition of Nb_3Sn antisite disorder is introduced. An interesting outcome of the experiment was that the same type of disorder is generated by ball milling as by neutron irradiation or by high temperature in the equilibrium situation.

In order to investigate whether this conclusion is more generally valid, we decided to perform ball-milling experiments on a compound which is known to exhibit a different type of atomic disorder at higher temperatures, viz., CoGa. This compound crystallizes in the *B*2 (CsCl) structure and has a wide homogeneity region, extending at low temperature from about 43 to 67 at. % Co. Previous studies on Co_xGa_{100-x} compounds[12-14] have pointed out that two types of antisite Co atoms, i.e., Co atoms on the Ga sublattice, should be distinguished: structural antisite atoms, introduced at the Co-rich side of the equiatomic composition, and thermal antisite atoms associated with the thermal disorder. The latter type of disorder is the so-called triple-defect disorder: the substitution of Co atoms on the Ga sublattice is combined with the formation of vacancies on the Co sublattice in a ratio 1:2. The substantial amount of vacancies connected with this type of disorder, is reflected in a decrease of the lattice parameter which is characteristic for triple-defect disorder. Magnetic studies on Co_xGa_{100-x} compounds[14-20] have shown that the Co antisite atoms are predominantly responsible for the magnetic properties. This appears to be associated with the formation of magnetic moments on magnetic centers formed by Co antisite atoms surrounded by eight nearest-neighbor Co atoms, situated on their own sublattice. Therefore, magnetic measurements may provide useful information regarding the concentration and distribution of antisite atoms in these compounds. On the other hand, the antisite atom concentration is obviously dependent on the heat treatment given to the samples and on the extent to which a particular high-temperature equilibrium state has been quenched, so that the results of various investigations are often difficult to compare.

In the present investigation, a comparison will be made between the results of magnetic measurements on ball-milled equiatomic CoGa and the results obtained on Co_xGa_{100-x} compounds with x ranging between 48 and 59 at. %. The magnetic properties of this series of compounds has successfully been analyzed in terms of magnetic centers associated with Co antisite atoms. The similar properties of ball-milled stoichiometric CoGa and unprocessed Co-rich Co_xGa_{100-x} clearly show that the ball-milling process gives rise to creation of Co antisite atoms. Lattice-parameter measurements unequivocally establish that triple-defect disorder is generated in the ball-milling process.

II. EXPERIMENTAL TECHNIQUES

The ball milling was carried out in a hardened-steel cylindrical 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 (Pulverisette 0, Fritsch), upon which the vial was mounted. To prevent oxidation, the milling was done in a glove box in a purified-argon atmosphere (with oxygen and water less than 5 ppm). All experiments with different milling times started from an amount of 0.5 gram powder prepared as described in Sec. IV A. The milling periods ranged from 2 to 32 h. X-ray diffraction patterns were taken at room temperature by means of a Philips vertical powder diffractometer using Cu $K\alpha$ radiation. The lattice parameter was calculated from x-ray diffraction patterns. For an accurate calculation of the lattice parameter, the samples for x-ray measurements were mixed with silicon powder as a standard. Compositional analysis of a sample milled for 20 h was performed on a Jeol JSM 840A scanning electron microscope with energy detector system. Annealing of the powder took place in a resistance furnace in a sealed quartz ampule filled with argon. The powder was wrapped in tantalum foil to protect the powder from a reaction with quartz.

Magnetic susceptibilities between 1.4 and 300 K in magnetic fields up to 1.3 T were measured with a pendulum magnetometer.[15] High-temperature susceptibility measurements, between 330 and 1100 K, were performed in a Faraday-type magnetometer[21] in fields up to 1.0 T. The sensitivity of both magnetometers is about 2×10^{-8} A m^2.

High field magnetization measurements at 4.2 K were performed in the Amsterdam High Field Installation[22] in which fields can be generated up to 42 T, constant within 10^{-4} during 0.1 s. The pulse shape can be electronically regulated. For magnetization measurements on metallic specimens, usually stepwise pulses are applied in which the field is constant during the steps for about 40 ms, a time long enough to let eddy currents in metallic specimens decay. In the present investigation, fields up to 35 T were used, regulated in 7 steps of 5 T. The sensitivity of this magnetometer is about 10^{-5} A m^2.

III. MAGNETIC PROPERTIES OF CoGa COMPOUNDS

A. Sample preparation

CoGa compounds containing 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, and 59 at. % Co, respectively, were prepared by melting together weighed amounts of 6N-purity Co and Ga in crucibles of recrystallized alumina. Before the melting, the crucibles were placed in silica tubes, which were then vacuum sealed. After reaching a temperature of about 1250 °C in a resistance furnace, the melts were kept at this temperature for about 20 min. Then, the tube was taken out of the furnace and air cooled. In general, visual inspection showed the thus obtained ingots to contain rather large holes and the melting procedure was repeated as often (usually 2 or 3 times) as was necessary to get rid of them. The ingots were annealed for 3 days at 830 °C for homogenization and subsequently for 14 days at 550 °C. By x-ray diffraction it was found that all compounds had crystallized in the $B2$ (CsCl) type of structure. No traces of a second phase could be observed.

B. Experimental results

The magnetic properties of the investigated CoGa compounds strongly depend on the chosen annealing temperature. To illustrate this we show in Fig. 1 the inverse susceptiblity as a function of temperature for the compound $Co_{53}Ga_{47}$. The filled circles correspond to data taken with increasing temperature on a sample annealed at 550 °C. The sample is paramagnetic at all temperatures measured. Above 900 K, the susceptibility is observed to increase with increasing temperature. The plus signs show that the susceptibility of the sample has strongly increased when it is remeasured, again with increasing temperature, after it has been cooled in the Faraday balance from 1100 to 300 K in about half an

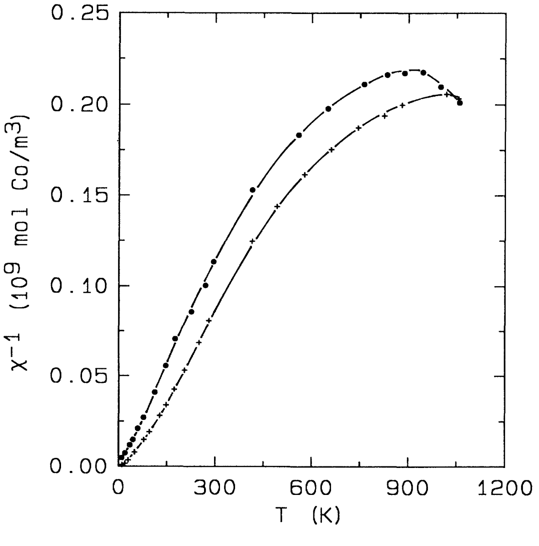

FIG. 1. The inverse susceptibility as a function of temperature for the compound $Co_{53}Ga_{47}$ up to 1100 K.

hour. The plus signs below 300 K correspond to data obtained on a different sample, annealed at 830 °C for homogenization and also furnace cooled. In contrast to the sample which after homogenization was annealed at 550 °C and which remains paramagnetic at low temperatures, this sample becomes ferromagnetic below 6 K.

The magnetic measurements reported in the present study, have been performed on CoGa compounds annealed at 550 °C. This temperature was selected because annealing at temperatures lower than 550 °C did not affect the magnetic properties. In Figs. 2 and 3 the inverse magnetic susceptibility is plotted for all compounds investigated. At lower temperatures, it is observed for all compounds that the magnetization does not depend linearly on the applied field. The temperature below which the magnetic isotherms display a certain amount of curvature, increases with increasing Co concentration. Since we were not able to measure initial susceptibilities directly, we derived them from M^2 versus B/M (Arrott) plots, a method commonly used for ferromagnetic compounds in the vicinity of the Curie temperature. After correction for a small, presumably spurious, spontaneous magnetization the Arrott plots were straight lines in the range of applied fields between 0.2 and 1.3 T and the values for the susceptibility and spontaneous magnetization could be derived as a function of temperature. As an example, the Arrott plots for $Co_{59}Ga_{41}$ at various temperatures are shown in Fig. 4. In this way, the compounds $Co_{57}Ga_{43}$, $Co_{58}Ga_{42}$, and $Co_{59}Ga_{41}$ were found to become ferromagnetic below 1, 70, and 136 K, respectively. The other compounds with Co concentrations of 56 at. % and lower remain paramagnetic at all temperatures.

The magnetic isotherms obtained at 4.2 K in fields up to 35 T are shown in Fig. 5. For all compositions, a strong tendency to saturation is observed. The Arrott plots corresponding to these isotherms are straight lines in the low field (below 2 T) region, but at higher field values saturation of M^2 occurs. Most of the samples have also been measured at 1.8 K. In fields above 1 T, there is no difference between the magnetization curves at 4.2 and 1.8 K.

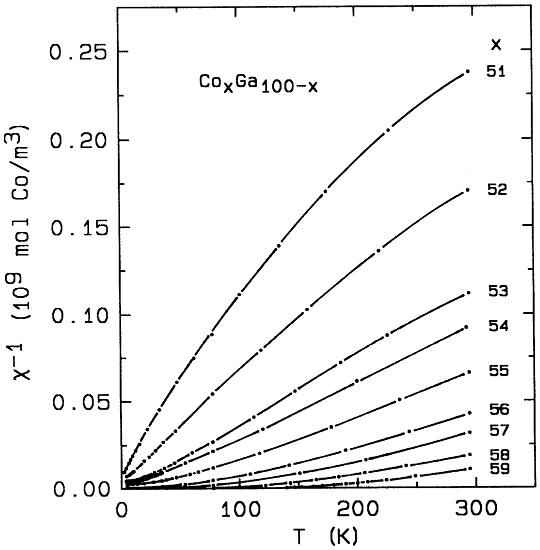

FIG. 2. The inverse susceptibility as a function of temperature for CoGa compounds with Co concentration from 50 at. % up to 59 at. % at temperatures up to 300 K.

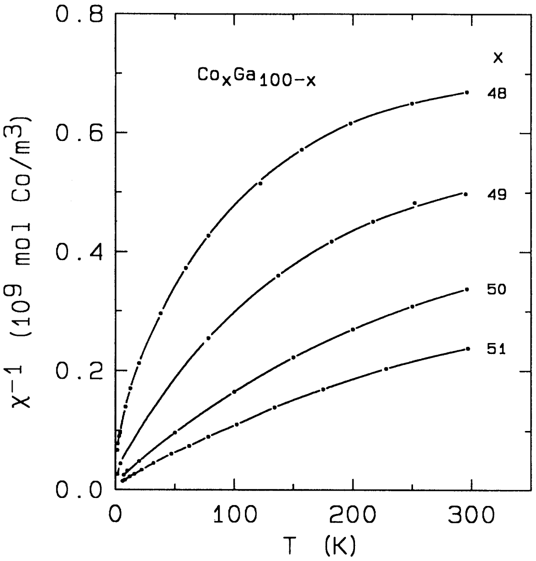

FIG. 3. The inverse susceptibility as a function of temperature for CoGa compounds with Co concentration from 48 at. % up to 51 at. % at temperatues up to 300 K.

C. Discussion

The susceptibility data were analyzed in terms of two contributions: a Curie-Weiss term and a temperature-independent Pauli susceptibility, so that

$$\chi=\frac{C}{T-\Theta}+\chi_0 . \tag{1}$$

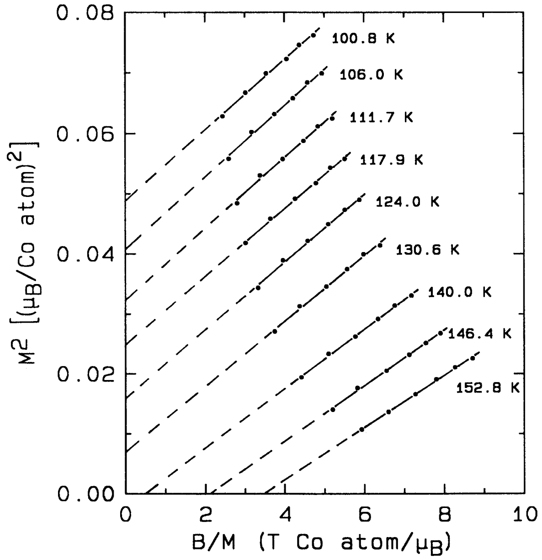

FIG. 4. Arrott plots of $Co_{59}Ga_{41}$ for different temperatures.

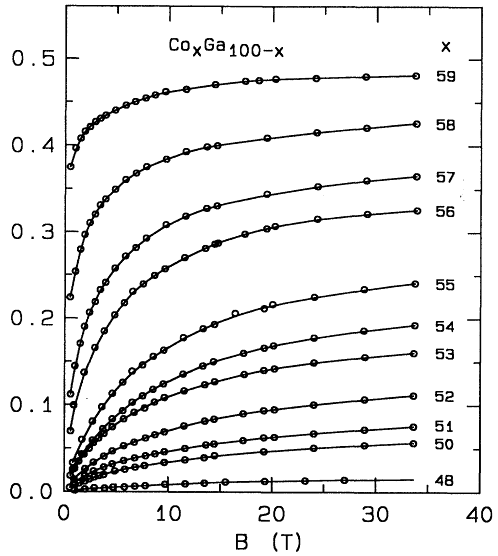

FIG. 5. Magnetization at 4.2 K as a function of applied magnetic field up to 34 T for all CoGa compounds prepared.

For Co concentrations up to 52 at. %, the observed temperature dependence of the susceptibility is properly described by the above relation. However, for higher Co concentrations, the experimentally observed tendency of the susceptibility to become constant at low temperatures is not accounted for by the above expression, so that at low temperatures deviations from this description occur. The Curie constants C for the compounds with Co concentrations larger than 56 at. % Co were determined from susceptibility measurements above 300 K. The results of the analysis are collected in Table I, together with the values of the magnetic moment per Co atom in 35 T. The Pauli susceptibilities χ_0 have been expressed in units m^3/mol of atoms, since both constituents contribute to the band states at the Fermi level. However, because the Ga atoms certainly do not carry a localized magnetic moment, we have expressed the Curie constants C in units m^3/mol of Co atoms, despite the fact that the main result of the present investigation will be that also not all Co atoms carry a moment. It can be read from Table I that both the Curie constant, C, and the moment in 35 T, M (35 T), increase strongly with increasing Co concentration. Figure 6 shows that both quantities vary roughly linearly with the Co content in the composition range between 52 and 55 at. % and that they both extrapolate to approximately zero at the equiatomic composition.

By a comparison of the macroscopic density to the lattice parameter and also by measuring thermal expansion and lattice parameter as a function of temperature,[12] it was demonstrated that CoGa exhibits so-called triple-defect disorder, i.e., the formation of Co antisite atoms combined with vacancies on the Co sublattice in a ratio 1:2. The degree of this disorder increases with temperature and even well-annealed samples retain some disorder due to the lack of atomic mobility below 550 °C. This is corroborated by the observed approximate vanishing of the magnetic moments at the equiatomic composition which confirms that the magnetic properties of CoGa intermetallic compounds are predominantly due to the excess (antisite) Co atoms residing on the Ga sublattice. The above experimental results suggest the formation of localized moments to be associated with magnetic centers consisting of an antisite Co atom and its eight nearest-neighbor Co atoms. The deviations from linearity in Fig. 6, occurring at Co concentrations around 50 at. %, indicate that antisite atoms are already present at the equiatomic composition and also at lower Co concentrations than the equiatomic composition. The Θ values (Table I) can be considered as the average value of the magnetic interactions between the magnetic centers in each compound. For the smallest Co concentrations, i.e., the largest average distance between the magnetic centers, the average value of the interaction has the antiferromagnetic sign. For these low Co concentrations, the formation of clusters, i.e., two or more magnetic centers of which the antisite atoms are nearest neighbors, can be neglected. For Co concentrations larger than 51 at. %, the interaction constant has the ferromagnetic sign. It is remarkable that, despite this, all compounds with Co concentrations between 51 and 56 at. % remain paramagnetic down to the lowest temperatures measured. This is very

TABLE I. The results of Pauli susceptibility χ_0, Curie constant C, magnetic moment M in 35 T, the paramagnetic Curie temperatue Θ, magnetic centers per Co atom, and antisite atoms per Co atom as calculated from Ref. 12.

Co concentration [at. %]	χ_0 [10^9 m^3/mol atom]	C [10^9 m^3/mol Co-atom]	M (35 T) [μ_B/Co-atom]	Θ [K]	Magnetic centers per Co atom	Antisite atoms per Co atom
48	0.56	100	0.017	−7.5	0.006	0.002
49	0.55	236		−6		
50	0.65	493	0.058	−5	0.020	0.020
51	0.81	790	0.077	−5	0.034	
52	0.73	1320	0.113	1	0.039	0.050
53	0.80	2060	0.162	15	0.056	
54	0.80	2340	0.195	40	0.067	0.080
55	0.80	3200	0.243	60	0.084	
56	0.80	4290	0.326	90	0.112	0.110
57	0.80	4880	0.367	145	0.127	
58	0.80	5640	0.427	190	0.147	

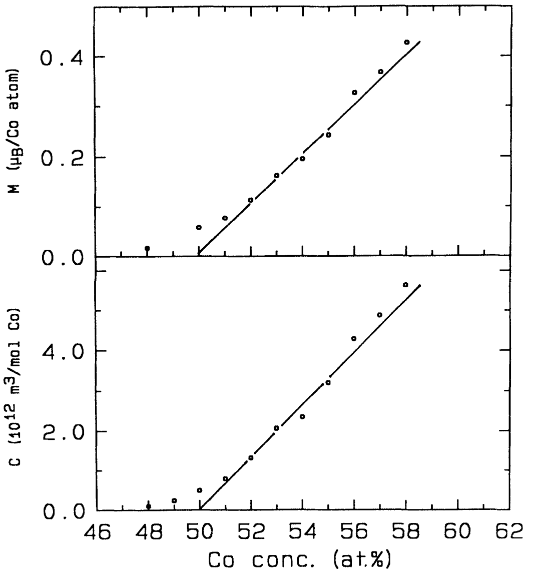

FIG. 6. The Curie constant (lower figure) and the magnetization in 35 T (upper figure) as a function of Co concentration.

likely a consequence of the competing ferro- and antiferromagnetic interactions between the magnetic centers in this concentration range. In Arrott-plot analyses, the samples with Co concentration larger than 56 at. % are found to order ferromagnetically.

The approximate linear concentration dependencies of C and M (35 T), at least in the composition range between 52 and 55 at. % Co strongly indicate that up to about 55 at. % Co the magnetic properties are mainly due to isolated magnetic centers. This suggests that in the annealing process at 550 °C the antisite atoms tend to occupy positions with maximum mutual distance. The minor deviations from linear concentration dependence above 55 at. % Co illustrate that the value of the magnetic moment of a cluster containing more magnetic centers varies approximately linearly with the number of magnetic centers present in the cluster.

Now, let us, for sake of simplicity, neglect the presence of thermal antisite atoms and assume that in compounds in the concentration range between 52 and 55 at. % Co, the structural antisite atoms form isolated magnetic centers as described above. In this case, from the straight line drawn in the upper panel of Fig. 6, a magnetic moment of $2.9\mu_B$ per magnetic center can be derived. It should be noted that the line drawn does not pass through zero at the equiatomic composition. At this composition, from the Pauli susceptibility of 0.65×10^9 m^3/mol atom, a value of $0.006\mu_B$/Co atom can be deduced for the moment induced by the field of 35 T. By means of the value of the magnetic moment of $2.9\mu_B$ per magnetic center, values for the number of magnetic centers per Co atom, as tabulated in Table I, can be derived from the values for M (35 T). Due to the neglect of the presence of thermal antisite atoms in this consideration, the value of $2.9\mu_B$ should be considered as an overestimation of the value for the moment per magnetic center. This implies that the values for the number of magnetic centers per Co atom, tabulated in Table I, may be somewhat too low. For comparison, the corresponding number of antisite Co atoms calculated from Ref. 12 is also given in Table I. From the crystal structure, it can easily be seen that, even if the antisite atoms are positioned at maximum mutual distance, the formation of clusters inevitably occurs if the Co concentration becomes larger than 56.25 at. %.

IV. BALL MILLING OF $Co_{50}Ga_{50}$

A. Sample preparation

A stoichiometric $Co_{50}Ga_{50}$ compound for ball-milling experiments was prepared in a similar way as the compounds for magnetic measurements. The only difference is that the ingot obtained by melting was subsequently arc melted to get rid of holes. The arc melting was performed several times under argon atomsphere to ensure homogeneity. The arc-melted button was crushed into powder and subsequently annealed at 550 °C for 64 h.

B. Experimental results

Figure 7 shows the high-field magnetization measurement of the stoichiometric CoGa compound milled for various periods. The field was applied up to 14 T and the measuring temperature was 4.2 K. In Fig. 8 the magnetization measured in a field of 14 T is presented as a function of milling time. From Fig. 8 it can be seen that for the first few hours of milling the magnetization increases rapidly with the milling time, whereas after milling periods longer than about 8 h the magnetization tends to saturate.

X-ray diffraction patterns for the unprocessed material and the materials milled for 6 and 32 h are shown in Fig. 9. It is observed that after milling the material still

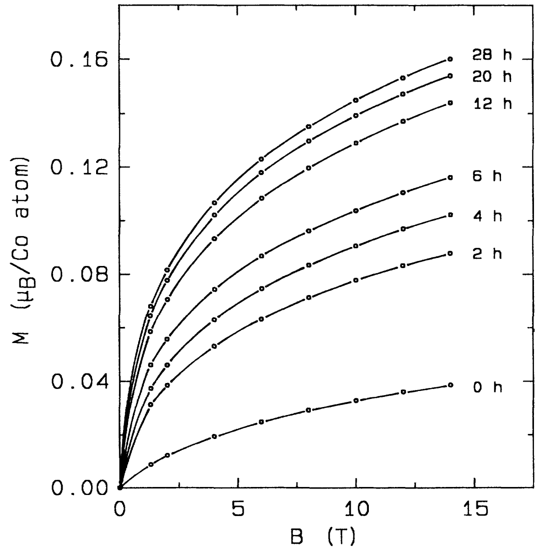

FIG. 7. Magnetization as a function of applied magnetic field up to 14 T for the equiatomic CoGa compound milled for various periods.

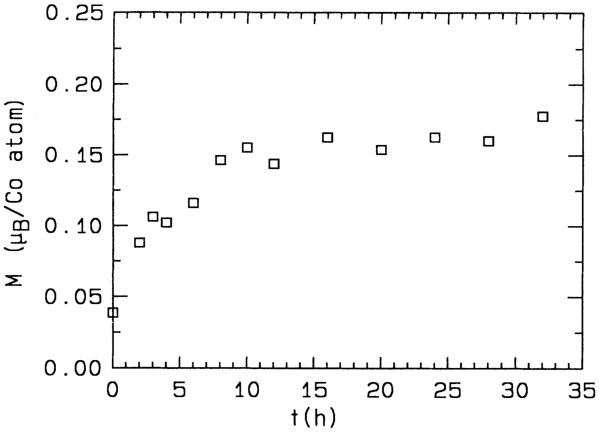

FIG. 8. Magnetization of $Co_{50}Ga_{50}$ at 14 T as a function of milling time.

remains in the $B2$ structure, whereas the intensities of the [100] and [210] superlattice reflections decrease. This is an indication that the material is disordered by ball milling. The relative change of the lattice parameter of CoGa as a function of milling time is presented in Fig. 10. As to be expected for triple defect disorder, the lattice parameter decreases. The lattice parameter for the unprocessed sample is 2.8856±0.0008 Å which is in close agreement with 2.8845±0.0002 Å observed by van Ommen[23] for the CoGa compound containing 50 at. % Co.

The microprobe analysis revealed that the sample milled for 20 h contains 50.7±1.4 at. % Co and 49.3±1.0 at. % Ga. Only 0.03 (±0.03) at. % Fe was detected, which could come from the steel tools. So, during the milling process the CoGa compound is almost not contaminated. Annealing the sample milled for 32 h at 550 °C for 115 h restores the magnetization and the lattice parameter to their original values. This proves that the process is reversible and that the increase of the magnetization during milling is not due to contamination or to the irreversible introduction of lattice defects.

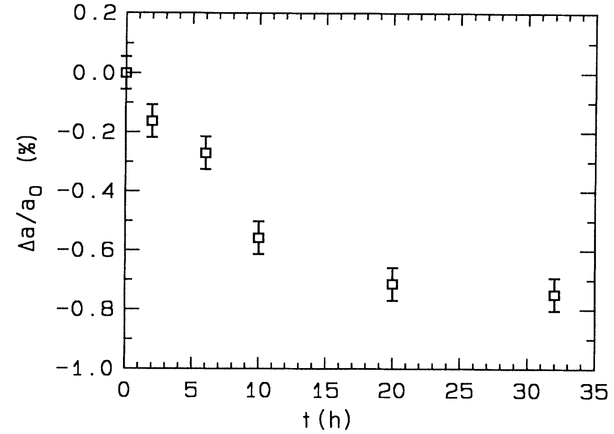

FIG. 10. Relative change of the lattice parameter of $Co_{50}Ga_{50}$ as a function of milling time.

For comparison with the experiment results on Co_xGa_{100-x} compounds presented in Sec. III B, susceptibility measurements were also performed on the ball-milled samples. The results for the inverse susceptibility as a function of temperature are given in Fig. 11. The curve for the unprocessed CoGa is the same as the curve for $Co_{50}Ga_{50}$ given in Fig. 2. The behavior for $Co_{50}Ga_{50}$ milled for 4 and 12 h shows similarity to the results for $Co_{54}Ga_{46}$ from Fig. 2, which are also presented in Fig. 11 by the crosses.

C. Discussion

From compositional analysis and from the fact that by appropriate annealing of the processed samples the lattice

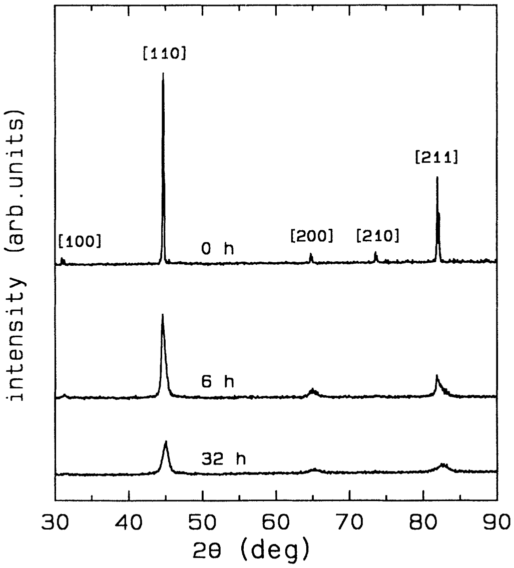

FIG. 9. X-ray diffraction patterns for of $Co_{50}Ga_{50}$ milled for different times.

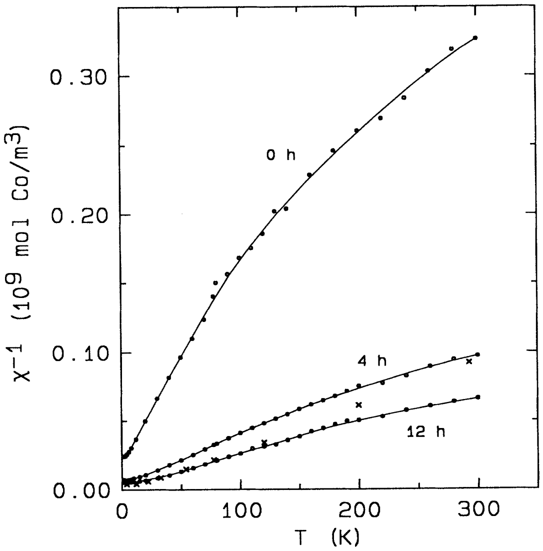

FIG. 11. The inverse susceptibility as a function of temperature for of $Co_{50}Ga_{50}$ milled for different periods. The crosses are results for as-prepared $Co_{54}Ga_{46}$.

parameter and magnetization are restored to the values of the unprocessed CoGa, we conclude that irreversible effects do not play a role. In contrast to some other compounds, CoGa remains crystalline under mechanical treatment. However, the decrease of the intensities of the superlattice reflections (Fig. 9) points in the direction of disorder. From the increase of the magnetization and the decrease of the lattice parameter with increasing milling time, it is concluded that mechanical attrition brings the material into a state of disorder, of the same type as the disorder generated in equilibrium at high temperatures, namely, triple-defect disorder.

Let us attempt to make this argument quantitative. In CoGa compounds, structural vacancies exist at compositions with less than 50 at. % Co. Besides, in all compositions we also find thermal vacancies.[12] The number of thermal vacancies increases with temperature and this effect is in particular manifest in the equiatomic compound. Remarkably, it turns out that in samples with Co content higher than or equal to 50 at. %, vacancies are also detected at room temperature. These are no structural vacancies, but vacancies that cannot be annealed out because of the lack of atomic mobility below a temperature of about 550° C. Actually, at room temperature, the samples are in the equilibrium state corresponding to a much higher temperature and therefore contain a certain amount of thermal vacancies and antisite Co atoms. This explains the nonzero magnetization in high fields of the equiatomic compound. From the work by Van Ommen *et al.*,[12] it is found that in this composition 2% of vacancies remain at room temperature. Since thermal vacancies and thermal antisite Co atoms are always formed in a ratio 2:1, a stoichiometric sample contains 1% of antisite Co atoms, which are primarily responsible for the magnetic properties of the compound. In order to make an estimate of the number of antisite atoms in our samples, let us first consider the magnetization of $Co_{54}Ga_{46}$ in a field of 14 T. From Ref. 18 we find a vacancy fraction in a sample of this composition of 0.68% at room temperature. The fraction of antisite atoms consists of the sum of structural antisite atoms (4%) and thermal antisite atoms (0.34%), which cannot be annealed out. From Fig. 5 we read a value of $0.15\mu_B$ per Co atom at 14 T. This means a value of $54\times 0.15/4.34=1.9\mu_B$ per antisite atom. In the same way we find for the $Co_{55}Ga_{45}$ compound also a value of about $1.9\mu_B$ per antisite atom, which is appreciably lower than the $2.9\mu_B$ derived in Sec. III C. This is due to the fact that full saturation has not yet been reached at 14 T. Furthermore, as explained in Sec. III C, $2.9\mu_B$ represents an overestimated value for the moment per antisite atom. From Fig. 8 we estimate the value of the magnetization for long milling times to be $0.16\mu_B$ per Co atom. With a value of $1.9\mu_B$ per antisite atom we obtain a fraction of $50\times 0.16/1.9\approx 4\%$ of antisite atoms in the stoichiometric sample after long milling periods. A fraction of 4% of antisite atoms is also in agreement with the measurements of the magnetic susceptibility presented in Fig. 11. From Fig. 11, however, it can be seen that the shapes of the two susceptibility curves for $Co_{54}Ga_{46}$ and CoGa milled for 12 h are different. Also, comparison of the high-field magnetization curves in Figs. 5 and 7 shows a different saturation behavior for the Co_xGa_{100-x} compounds and for the disordered equiatomic CoGa compound. This may be explained as follows. In the Co_xGa_{100-x} compounds with $x>50$, the antisite Co atoms are surrounded by eight nearest-neighbor Co atoms, whereas in the ball-milled equiatomic CoGa compound, the antisite Co atoms are surrounded by less than eight nearest-neighbor Co atoms together with the vacancies. This reduced number of Co nearest neighbor is due to the fact that the appearance of one Co atom on the Ga sublattice always corresponds with the creation of two vacancies on the Co sublattice.

We now examine whether this concentration of antisite atoms is consistent with the lattice-parameter measurements as a function of milling time (Fig. 10). A fraction of 4% antisite atoms implies a fraction of 8% vacancies. According to Van Ommen,[23] the unprocessed material contains a fraction of 2% vacancies and therefore a fraction of 1% antisite atoms. Edelin[13] studied the behavior of the lattice parameter of quenched samples of different compositions in relation to the number of vacancies and antisite atoms. He arrived at the following result:

$$a=a_0[1+\tfrac{1}{3}(\Omega_v-1)c_v+\tfrac{1}{3}(\Omega_{as}-1)c_{as}] , \qquad (2)$$

where a is the lattice parameter, a_0 the lattice parameter for the compound without defects. Ω_v is the vacancy volume relative to the atomic volume and equals 0.69 according to Edelin,[13] Ω_{as} is the same ratio but now for the antisite atom (=0.89) and c_v and c_{as} are the fractions of vacancies and antisite atoms, respectively. Applying Eq. (2) to the unprocessed sample (with fractions of vacancies and antisite atoms of 2% and 1%, respectively) and to those milled for long times (corresponding fractions 8% and 4%, respectively), we calculate a decrease of the lattice parameter of about 0.7% for long milling times. This is in excellent agreement with the results of the lattice-parameter measurements as given in Fig. 10. From the above results, it is clear that the numbers of antisite atoms and vacancies derived from the magnetic measurements is consistent with the results of measurement of the lattice parameter. This proves that by mechanical attrition CoGa disorders and that the disorder is of the same type as thermal disorder.

In the compound Nb_3Sn,[11] we have been able to evaluate the ballistic-jump frequency, i.e., the rate at which a nearest-neighbor pair of Nb and Sn atoms is exchanged by mechanical impact. This ballistic-jump frequency was found to be equal to $5\times 10^{-7}s^{-1}$. This means that after 10 000 s of milling, the fraction of Nb-sublattice sites occupied by Sn atoms is 2%. From the lattice-parameter measurements presented in Fig. 10 and with the aid of Eq. (2), it turns out that in CoGa after 10 000 s of milling, about 1% of Ga-sublattice sites are occupied by Co atoms. This indicates that the ballistic-jump frequency in CoGa is of similar order of magnitude as in Nb_3Sn.

By comparison of the fraction of vacancies formed by mechanical attrition to that created by temperature, we are able to estimate the temperature at which the same amount of disorder would exist as generated by attrition.

From Ref. 23 we arrive at a corresponding temperature of about 1100 °C. From the estimated temperature of about 1400 K, we can estimate the energy stored in the material due to mechanical attrition to be about 10 kJ/mol.

V. CONCLUSIONS

Mechanical attrition of CoGa generates triple-defect disorder: vacancies on the Co sublattice combined with antisite Co atoms on the Ga sublattice in a ratio of 2:1. This is the type of disorder also found at high temperatures in thermodynamic equilibrium. The triple-defect content monitored by magnetic measurements agrees excellently with that derived from the measurement of the decrease of the lattice parameter. The disorder generated by mechanical attrition does not precede a phase transition: the material remains *B*2 type, also for long milling periods. The final state of disorder obtained corresponds to the equilibrium state at 1100 °C. It appears that mechanical attrition in a ball mill, which is a seemingly crude and rough technique, induces well-defined metastable states.

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