Changes in the structural and magnetic properties of $GdIr_2$ with the milling process

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Both ac magnetic-field and dc low and high magnetic-field measurements, have been used, to study the magnetic property changes in relation to the structural changes, induced by ball milling of $GdIr_2$, which is, in the ordered state, a ferromagnetic cubic Laves phase compound. A ferromagnetic transition is shown to be present for all samples, the value of which depends linearly on the Gd-Gd distance, because of the negligible influence of the $5d$ electrons of Ir on the exchange interaction between the Gd atoms. After intermediate and longer periods of milling, antiferromagnetic interactions are induced, as a consequence of Gd atoms being transferred to the Ir sublattice. This is shown to result in spin-glass-like behavior: a reentrant spin glass appears to be created. [S0163-1829(98)07145-8]

I. INTRODUCTION

Mechanical milling of intermetallic compounds can induce changes in all kinds of properties. A study of the changes of the magnetic behavior of some cubic GdX_2 Laves phase (C15 or $MgCu_2$) compounds gives remarkable results. For example, both $GdAl_2$ and $GdPt_2$ disorder in a vacancy type of disorder under milling which was termed quadruple-defect disorder.[1,2] Apparently, this leads to $GdAl_2$ becoming a spin glass, whereas an increasing Curie temperature is found while milling $GdPt_2$. Therefore, we may conclude, that the magnetic properties do not only depend on the type and degree of disorder that is generated in the compound, but also on the electronic properties of the nonmagnetic element. The *p*-electron character of Al enables it to highly influence the interaction between Gd atoms, when it is substituted on the Gd sublattice. The *p* electrons of Al are able to introduce antiferromagnetic coupling between Gd atoms, possibly in a way similar to superexchange, which can lead to spin-glass behavior, as found. In contrast, Pt is a $5d$ element and the $5d$ electrons of rare earths have been found to play a much smaller role in the exchange interaction between the rare earth moments.[3] Therefore, the interaction between the Gd atoms is mainly influenced by the change in the distance between the Gd atoms as a consequence of the changing lattice parameter, which even resulted in a linear relation between the lattice parameter and the Curie temperature.[2]

Ir is also $5d$ metal and the cubic Laves phase compound $GdIr_2$ has also been shown to disorder in quadruple-defect disorder for short milling times,[4] but the ordered compound has a Curie temperature of about 88 K,[3] which is reasonably higher than the value of 33 K that has been found for ordered $GdPt_2$.[2] The reason for this difference can still be found in the electronic structure. It turns out that the participation of the $5d$ electrons of Gd is smaller in $GdPt_2$ than in $GdIr_2$,[5,6] which causes the significant difference in Curie temperatures.

For longer milling times, $GdIr_2$ starts to disorder in anti-site disorder,[4] which means that not only Ir atoms are being transferred to the Gd sublattice, but that now, Gd atoms are also substituting on the Ir sublattice. Therefore, one expects that the magnetic properties will not only be influenced by the changing Gd-Gd distance, but also by the more significant change in surroundings of a number of Gd atoms, because of their transfer to the Ir sublattice. Here, a study of the changes of the magnetic behavior of $GdIr_2$ under milling will be presented. It is the aim of this work to show that drastic changes occur in this behavior, when the compound is disordered by milling on an atomic level and to suggest an interpretation of the observed phenomena rather than to present an unambiguous explanation.

II. EXPERIMENTAL TECHNIQUES

$GdIr_2$ was prepared in the stoichiometric composition, by arc melting weighted amounts of pure gadolinium and iridium in a purified argon atmosphere. Arc melting was repeated a few times in order to obtain a homogeneous sample. The button was crushed to powder and put in a molybdenum crucible, which was placed in a quartz tube, sealed under 300 mbar of argon, to be sure that all defects, created by crushing the button, would be removed. The sample was annealed in this way for four days, at a temperature of 893 K.

Milling of the sample was carried out in a stainless steel vial with a tungsten carbide bottom. The inner diameter of the vial was 6.5 cm. The vial was mounted upon a water-cooled vibrating frame (Fritsch: Pulverisette 0), which kept one hardened-steelball in motion. The diameter of this ball was 6 cm. Continuous pumping during milling, prevented the powder from being contaminated by oxygen and nitrogen. The vacuum was kept below 10^{-6} mbar. The starting amount of material was about 4.5 g.

The crystallite size was determined from the broadening of the peaks in the x-ray pattern, that was taken in a vertical Philips powder diffractometer using Cu $K\alpha$ radiation. Silicon was used as a standard. The same measurements were used to determine the lattice parameter.

ac susceptibility measurements were performed by self-designed equipment, applying a measuring field of 0.06 mT at a frequency of 109 Hz. The temperature was lowered from room temperature down to 4.2 K.

Low dc field-magnetization measurements were performed by a superconducting quantum-interference device (SQUID), in which magnetic fields from -5 to 5 T can be

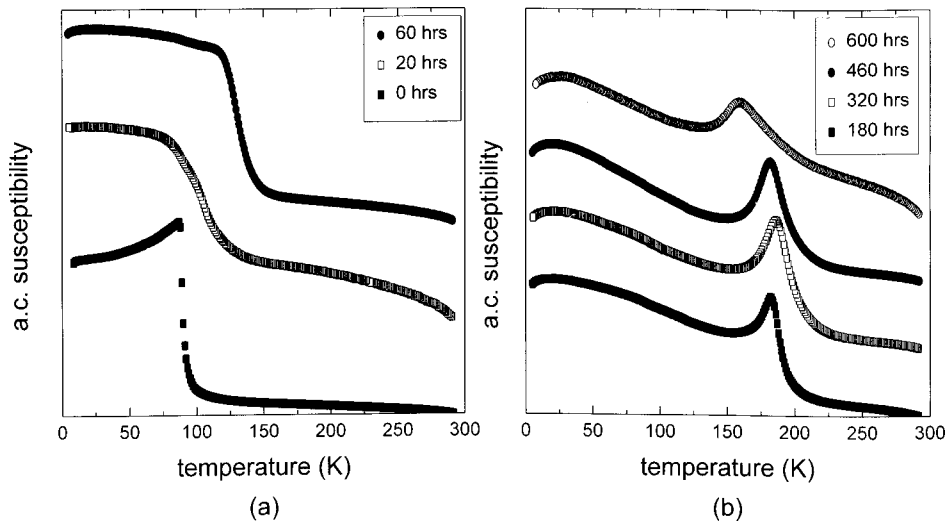

FIG. 1. Temperature dependence of the ac susceptibility of $GdIr_2$, for short (a) and intermediate and long (b) milling times.

generated by a superconducting magnet. Magnetization curves were measured in various small fields, from 5 up to 200 K. These measurements were performed both, after having the sample cooled without the measuring field on [zero field cooled (ZFC)] and, after having it cooled in the measuring field [field cooled (FC)].

High dc field magnetization measurements were performed on the Amsterdam High Field Installation at a temperature of 4.2 K. Stepwise field profiles from 21 down to 1.3 T was applied.

III. RESULTS AND DISCUSSION

In Figs. 1(a) and 1(b), the ac susceptibility plots of $GdIr_2$ are given, for various milling times. From Fig. 1(a), it is observed that unmilled $GdIr_2$ (bottom curve) is a ferromagnet at lower temperatures with a transition temperature, (Curie temperature) T_c, of 89.1 K (see also Fig. 2) which is in good agreement with the value reported by Buschow.[3] (The value for the Curie temperature was defined as the minimum of the derivative of the ac susceptibility curve.) For short milling times, the ferromagnetic transition is observed to broaden somewhat and to shift to higher temperatures. For longer milling times [see Fig. 1(b)] the broadening of the transition continues, while the Curie temperature still increases, up to a value of 192.4 K after 320 h of milling, but starts to decrease thereafter. It is also observed that the shape of the curve is changing more significantly: The transition takes the character of a maximum and at very low temperatures, below about 25 K, a second anomaly becomes visible.

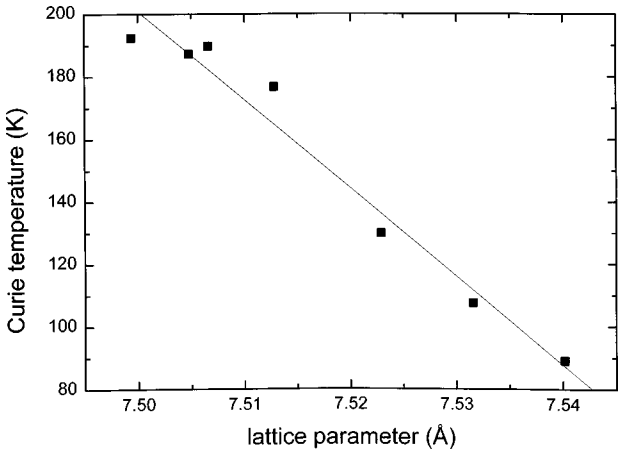

FIG. 2. Variation of the Curie temperature of $GdIr_2$ as a function of the lattice parameter and a least-square fit to the data (solid line).

The changes of the magnetic properties can not be a consequence of the reduction of the crystallite size, because $GdIr_2$ becomes nanocrystalline already after 20 h of milling, when a crystallite size of about 14 nm is found. For longer milling times, an only slightly smaller, final value of about 10 nm is reached. Therefore, the magnetic property changes must be related to structural changes.

In Fig. 2, the Curie temperature is plotted vs the lattice parameter. It can be seen that, just as was found for $GdPt_2$, the relation between the Curie temperature and the lattice parameter appears to be approximately linear, which is not very surprising if the value of the Curie temperature changes mainly as a consequence of the changing distance between Gd atoms, because of the very small influence of the $5d$ electrons of Ir on the exchange interaction between the Gd atoms. The present case gives even stronger evidence for this, as the linear relation remains also valid when antisite defects start to be created[4] instead of quadruple defects. In the case of milling of $GdPt_2$ antisite defects were not found to be induced, instead we kept on creating quadruple defects and increasing the Curie temperature under milling, even up to periods of 2420 h.

In order to obtain a better understanding of the magnetic properties of $GdIr_2$ after long milling times, especially of the anomaly that appears at low temperatures, very low dc magnetic-field measurements were performed on the samples milled for 460 and 600 h. The measurements were taken both after being cooled in zero field (ZFC) and after being cooled in the measuring field (FC). The results of these measurements are plotted in Figs. 3(a)–3(c) and 4(a)–4(c).

The ZFC curve of the sample milled for 460 h taken in 10 mT, Fig. 3(a), shows two anomalies, at about 20 and 150 K, which correspond rather well to the maxima that were observed in the ac susceptibility curve. At low temperatures,

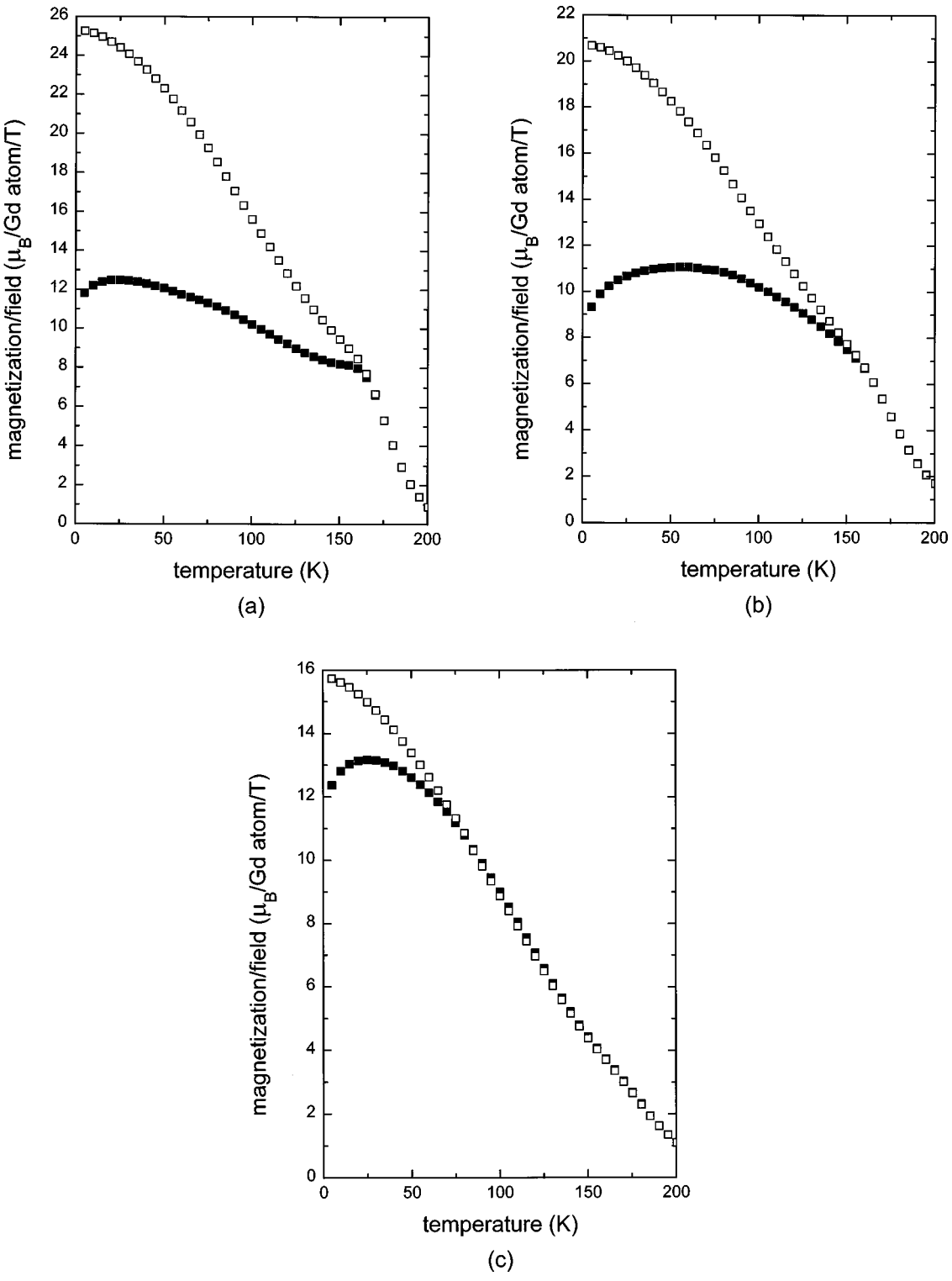

FIG. 3. ZFC (closed symbols) and FC (open symbols) magnetization/magnetic field vs temperature curves of $GdIr_2$ milled for 460 h, measured in fields of 10 mT (a), 20 mT (b), and 50 mT (c).

the FC curve can be observed to be located appreciably above the ZFC curve, up to about 160 K, where the curves start to coincide. In higher fields, Figs. 3(b)and 3(c), the anomaly at high temperature disappears completely and the curves coincide at lower temperatures, already. Both, the difference in ZFC and FC magnetization curves and the decrease of the coincidence temperature at higher fields are characteristic of spin glasses but also of superparamagnets. If the material would indeed have become a superparamagnet, clusters of Gd atoms would have to be present in an Ir matrix. This situation is very unlikely, because the x-ray pattern of this sample, which has been published in Ref. 4, still shows too many characteristics of the original crystalline structure (at least four peaks can still be distinguished). Therefore, the possibility that the material has become a superparamagnet can be ruled out and it must be concluded

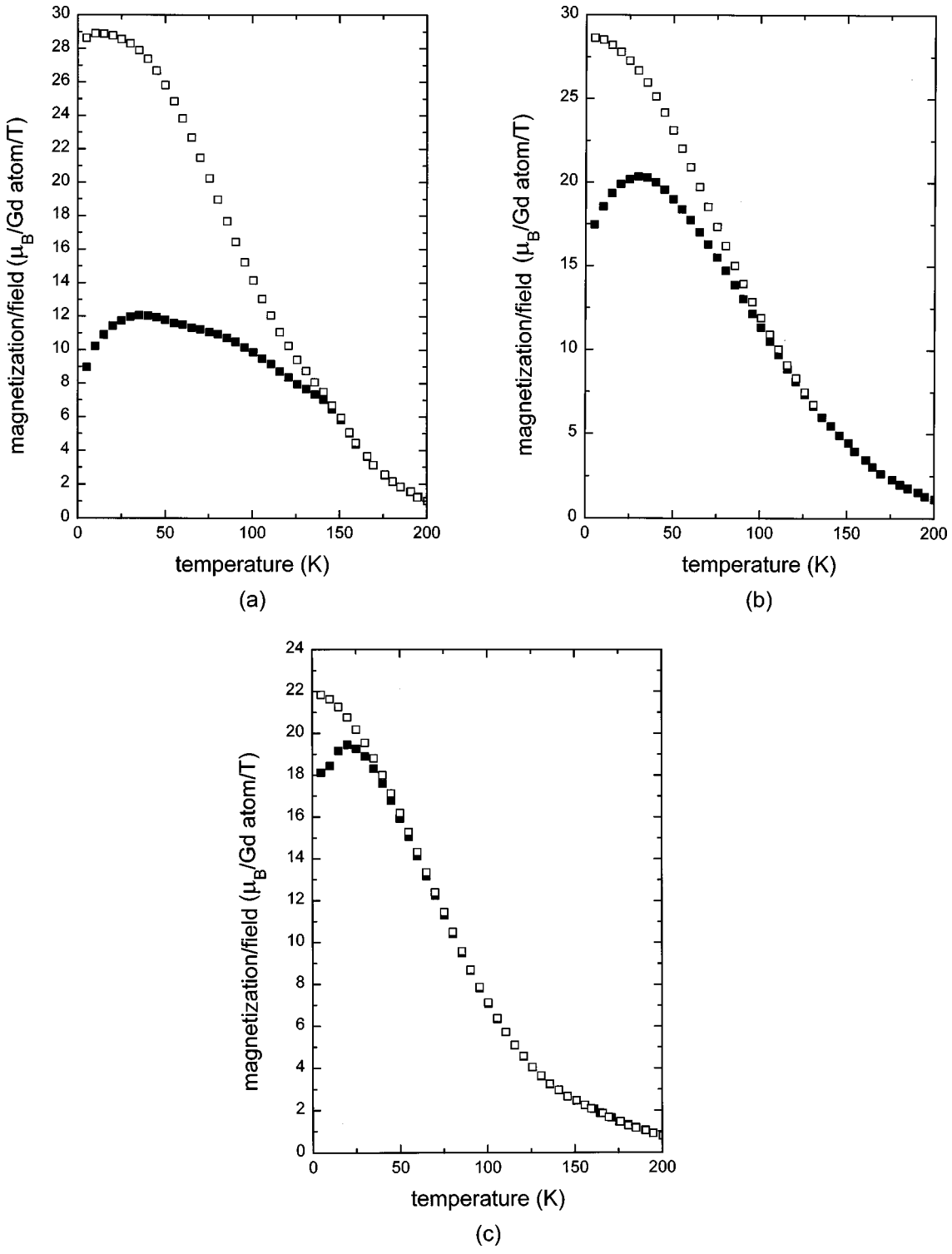

FIG. 4. ZFC (closed symbols) and FC (open symbols) magnetization/magnetic field vs temperature curves of $GdIr_2$ milled for 600 h, measured in fields of 10 mT (a), 20 mT (b), and 50 mT (c).

that it behaves, at least, spin-glass-like. The anomaly or maximum at low temperatures must thus be assigned to be the freezing temperature T_f of the spin-glass transition.

Figures 4(a)–4(c) show almost the same results as Figs. 3(a)–3(c) but the low-temperature anomaly is somewhat sharper. Here, it can also be seen clearly, that the freezing temperature shifts to smaller values when higher fields are applied, which is also characteristic of spin-glass behavior.

In Fig. 5(a) high-field magnetic measurements are shown. The unmilled sample is ferromagnetic with a saturation moment of about $7.4\mu_B$/Gd atom. This value is somewhat higher than reported by other authors,[3,7] but is still rather close to the free-ion saturation moment of $7\mu_B$/Gd atom.

In order to obtain spin-glass behavior, both ferromagnetic and antiferromagnetic interactions need to be present. Therefore, if we did indeed create a spin glass, antiferromagnetic interactions must have been induced in some way by ball milling. From Figs. 5(a) and 5(b), the samples were found to

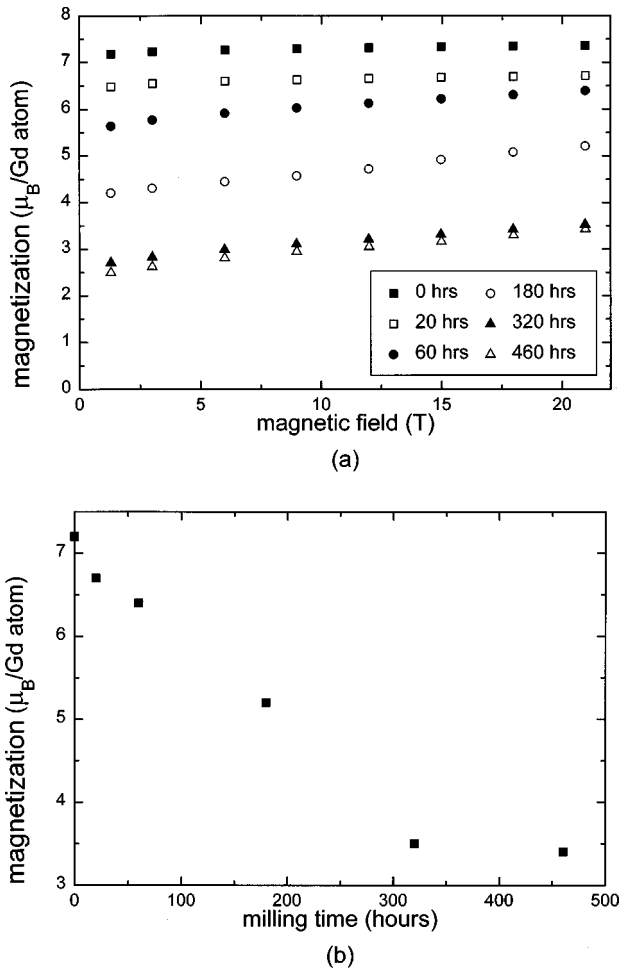

FIG. 5. High-field magnetization curves of $GdIr_2$ after various periods of milling, measured at 4.2 K (a) and the corresponding magnetization values at 21 T as a function of milling time (b).

become less and less ferromagnetic under milling, which can be concluded from the drastic reduction of the magnetization at 21 T [Fig. 5(b)], and from the fact that the samples milled for 60 h and longer do not saturate anymore in fields up to 21 T [Fig. 5(a)]. It is therefore concluded also from these measurements, that ball milling of $GdIr_2$ does indeed induce antiferromagnetic interactions. It is very unlikely that this is only due to the transfer of Gd atoms to the Ir sublattice. The significant suppression of the moment at 21 T, could only have been induced if a rather huge amount of Gd atoms was transferred. That is believed to be impossible without generating a phase transformation, which was not observed in the x-ray patterns.[4] The transfer of Ir atoms to the Gd sublattice probably influences the interactions more than concluded before. This would also explain the reduction of the saturation moment after relatively short milling times already, where (almost) only quadruple defects are expected to be present.

A more detailed study of the observed transitions, with the aid of scaling plots, such as Belayachi, Dormann, and Noguès performed, for example,[8] would probably give a better understanding of the magnetic behavior of mechanically milled $GdIr_2$. However, our data are, unfortunately, insufficient to perform a similar analysis. Combining the results of our measurement, it is concluded that $GdIr_2$, milled for 460 h and longer, exhibits spin-glass-like behavior, but apart from that, it also shows ferromagnetic behavior. Because of the presence of both features, we are, most likely, dealing with a so-called reentrant spin glass.

IV. CONCLUSIONS

The formation of defects in $GdIr_2$, as a result of mechanically milling of the ordered compound, induces significant and remarkable changes of the magnetic properties of the alloy. The changing of the Curie temperature of $GdIr_2$, under milling, can be completely attributed to the changing of the lattice parameter, and thus of the Gd-Gd nearest-neighbor distance, as a result of the introduction of defects. The relation between both changes is therefore approximately linear. The substitution of Ir on the Gd sublattice has not been found to play a significant role in this.

The introduction of both quadruple and antisite defects suppresses the saturation moment of the material. The transfer of Gd atoms to the ''wrong'' (i.e., Ir) sublattice, when antisite defects are formed, eventually leads to the appearance of an anomaly at low temperature. This anomaly has been identified as the freezing temperature of a spin-glass transition, so that after relatively long milling times, $GdIr_2$ has, apparently, been transformed into a reentrant spin glass.

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