# Characterization of magnetic phase transitions in $PrMn_2Ge_2$ compound investigated by magnetization and hyperfine field measurements

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The magnetic properties of $PrMn_2Ge_2$ compound have been investigated by perturbed $\gamma - \gamma$ angular correlation (PAC) spectroscopy using $^{111}In(^{111}Cd)$ as probe nuclei as well as by magnetization measurements. This ternary intermetallic compound exhibits different magnetic structures depending on the temperature. The magnetic ordering is mainly associated with the magnetic moment of 3*d*-Mn sublattice but at low temperatures a magnetic contribution due to ordering of the magnetic moment from 4*f*-Pr sublattice appears. PAC results with $^{111}Cd$ probe nuclei at Mn sites show that the temperature dependence of hyperfine field $B_{hf}(T)$ follows the expected behavior for the host magnetization, which could be fitted by two Brillouin functions, one for antiferromagnetic phase and the other for ferromagnetic phase, associated with the magnetic ordering of Mn ions. Magnetization measurements showed the magnetic behavior due to Mn ions highlighting the antiferromagnetic to ferromagnetic transition around 326 K and an increase in the magnetization around 36 K, which is ascribed to Pr ions ordering.  [http://dx.doi.org/10.1063/1.4974025]

## I. INTRODUCTION

Intermetallic compounds in the $REMn_2Ge_2$ family, where RE is a rare-earth element, have been studied by various techniques, such as neutron diffraction, magnetization, Mössbauer spectroscopy and resistivity measurements, in order to investigate their magnetic properties. These studies have shown multiple magnetic transitions in these compounds mainly due to Mn sublattice. They are well known to exhibit transitions from antiferromagnetic (AFM) to ferromagnetic (FM) ordering near room temperature.[1,2] Moreover, some compounds of this family have been reported to show magnetic ordering due to RE sublattice. $REMn_2Ge_2$ compounds crystallize in the prototype structure of $ThCr_2Si_2$ with $I4/mmm$ space group[3] where the RE, Mn and Ge atoms are stacked along the c-axis in the layered sequence RE-Ge-Mn-Ge-RE. In the specific case of $PrMn_2Ge_2$ an AFM ordering of Mn spins was reported to occur at 415 K which changes to FM ordering at 336 K when temperature decreases, and below 40 K, the Pr sublattice is observed to couple ferromagnetically to the Mn spins.[4–6] Layer-structured magnetic materials have raised interest in the recent years since the discovery of magnetocaloric effect (MCE).[7] In materials presenting MCE, the layered structure as well as the

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interlayer distances play a significant role in determining their magnetic and MCE properties. As a consequence, understanding the fundamental properties (e.g. the magnetic ordering and its origin) of layered materials such as $PrMn_2Ge_2$ has became of increasing importance.

The magnetic phase transitions are important in intermetallic materials because they are essential to deeper understanding of the systems and to determine their technological application. All the techniques cited above were used to characterize the magnetic phase transitions with high precision. Perturbed $\gamma - \gamma$ angular correlation (PAC) spectroscopy is a technique for the local investigation, and allows the study of specific sites in the crystal structure. Depending on the probe nuclei used for PAC spectroscopy we can define whether the transition temperature is related to ferromagnetic or antiferromagnetic transition. For example in the study of $LaMn_2Si_2(Ge_2)$ compounds by PAC spectroscopy with $^{140}$Ce probe defined the ferromagnetic transition while PAC measurements with $^{111}$Cd probe defined the antiferromagnetic transition.[8,9]

In this work we have investigated the magnetic behavior of intermetallic compound $PrMn_2Ge_2$ using magnetization measurements and measurements of the magnetic hyperfine field ($B_{hf}$) using the perturbed $\gamma-\gamma$ angular correlation (PAC) spectroscopy. Magnetization measurements were performed to characterize the magnetic behavior of host. PAC spectroscopy is a local study and we used this technique to measure the hyperfine field at Mn position using $^{111}$Cd as nuclear probe. The behavior of $B_{hf}$ as a function of temperature has been studied in the temperature range from 20 K to 480 K. This permitted determination of the Néel and Curie temperatures.

## II. EXPERIMENTAL PROCEDURE

$PrMn_2Ge_2$ was prepared by arc-melting the constituent elements (Pr =99.9%, Mn, Ge = 99.999% purity) in the stoichiometric proportions in pure argon atmosphere. A 5 wt% excess of Mn was used because a small part of Mn was found to be lost during arc melting. After melting, the resulting ingot was annealed in vacuum at 800 $^0$C during 24 hours. The crystal structure of the compound was determined by X-ray diffraction (XRD) at room temperature. The results were analyzed by Rietica software[10] that uses the Rietveld method and the result of residual of least-squares refinement Rp = 7.62. The analysis showed that the sample crystallized in the expected tetragonal structure of $ThCr_2Si_2$ in a single phase corresponding to $I4/mmm$ space group (see Fig. 1). The resulting lattice parameters were $a = b = 4.126(3)$ Å and $c = 10.924(5)$ Å in agreement with previously reported values.[11]

After structural characterization, a part of the sample was separated for the PAC measurements with $^{111}$In($^{111}$Cd) nuclear probe. PAC measurements using $^{111}$Cd probe nucleus are important in this compounds because the major fraction of $^{111}$Cd probes are found to substitute Mn sites in the crystal

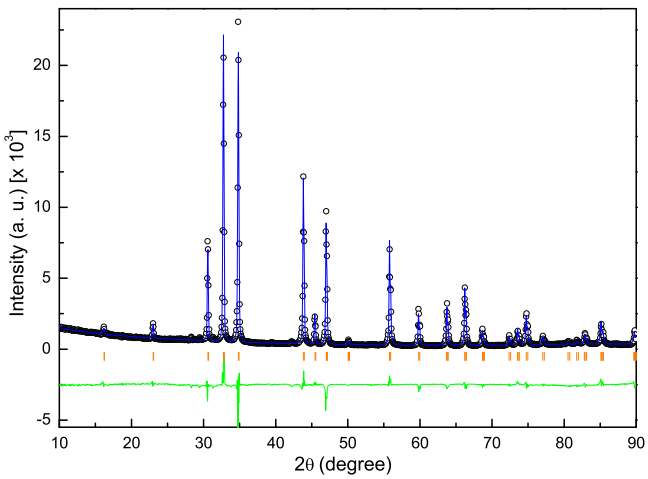


FIG. 1. X-ray diffraction spectra of $PrMn_2Ge_2$ compound. Solid lines are the fit to the experimental data using the Rietveld method.

lattice and, consequently, such measurements help in determining the arrangement of the Mn atoms in both antiferromagnetic and ferromagnetic phases as well as make it possible to determine the Néel temperature ($T_N$) as the $B_{hf}$ at Mn position vanishes.

A small quantity (20 - 30 $\mu$Ci) of carrier-free $^{111}$In was deposited on a small part of the sample and then re-melted in the arc furnace. The resulting ingot was sealed in a quartz tube in helium atmosphere and annealed at 850 $^0$C for 20 hours. PAC measurements were carried out with a four $BaF_2$ detector spectrometer and associated conventional fast-slow electronic setup to measure the delayed gamma-gamma coincidences. The gamma cascade of 171-245 keV in $^{111}$Cd populated from the electron capture decay of $^{111}$In has been used for PAC measurements. The Measurements were carried out in the temperature range 20-480 K using a closed loop helium cryogenic system. Description of the method as well as details about the PAC technique can be found elsewhere.[12,13]

The PAC measurements permitted the determination of Larmor frequency $\omega_L = \mu_N g B_{hf}/\hbar$, where $\mu_N$ is nuclear magneton and, since the g-factor of the probe nucleus is known, the calculation of the magnetic hyperfine field $B_{hf}$ is possible. PAC measurements in this compound also allowed to identify and characterize magnetic phase transitions.[8,12] The other part of sample, was used for magnetization measurements. The equipment used was a commercial Vibrating Sample Magnetometer (PPMS, QD) with an applied magnetic field of 100 Oe. Magnetization as a function of temperature was obtained using zero-field-cooled (ZFC) and field-cooled (FC) procedure.

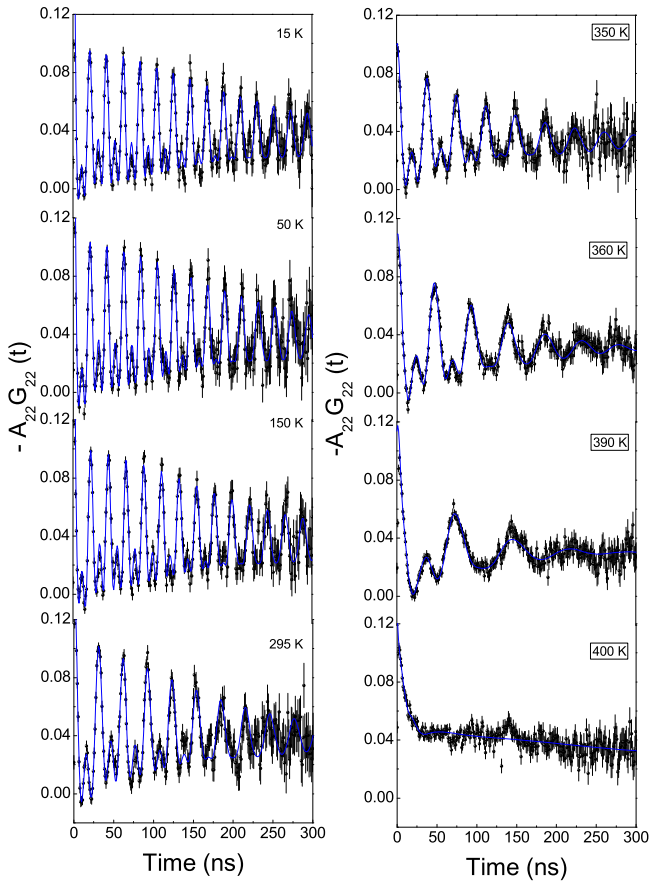


FIG. 2. Perturbation functions for $PrMn_2Ge_2$ with $^{111}$Cd probe nuclei measured at various temperatures. Solid lines are the least squares fit of the theoretical functions to the experimental data.

## III. RESULTS AND DISCUSSION

PAC spectra with $^{111}$Cd below 400 K were fitted with a model using a combined magnetic dipole and electric quadrupole interaction. The results at room temperature show a well defined magnetic dipole interaction ($\nu_M \sim 32.701(45)$ MHz) and a weak axially symmetric electric quadrupole interaction ($\nu_Q \sim 3.413(221)$ MHz) with delta (1.86(52)%). PAC spectra shown in Fig. 2. were measured at different temperatures in the range of 20 K-480 K. In the analysis of PAC data it was assumed that the $^{111}$Cd probes replace Mn atoms in $PrMn_2Ge_2$ intermetallic compound. This assumption is based on the consideration of higher chemical affinity of $^{111}$In for Mn rather than for Pr or Ge atoms as well as on the results of previous study.[8,14]

Fig. 3 shows results for magnetization and for the magnetic hyperfine field at $^{111}$Cd probe nuclei in a wide range of temperature in the $PrMn_2Ge_2$ intermetallic compound. The temperature dependence of $B_{hf}$ was fitted with two Brillouin functions (both for S=5/2), one for the antiferromagnetic phase and the other for the ferromagnetic phase. From the first fit to the Brillouin function, values of $B_{hf}(0) = 20.4(1)$T and $T_N = 400.3(1)$ K were precisely determined. The fit of the second Brillouin function in the temperature range below 326 K (ferromagnetic phase) is not quite obvious at the first sight. The existence of an antiferromagnetic to ferromagnetic phase transition with $T_C = 326.2$ K is clearly indicated by the magnetization measurements and this was therefore used in the fit of the second Brilloin function. The behavior of the magnetic field as a function of temperature presents a gradual ordering of the Mn sublattice as temperature decreases until near saturation. In this case therefore, the antiferromagnetic to ferromagnetic transition detected by PAC measurements is not a very sharp transition in contrast to the magnetization measurements. Mössbauer spectroscopy results[15] for $PrMn_2Ge_2$ doped with 2% of $^{57}$Fe clearly show the antiferromagnetic to ferromagnetic transition with a magnetic hyperfine field of around 12 T in the saturation region (although the lowest temperature shown is near 80 K). The difference in $B_{hf}$ is due to the $^{57}$Fe probe which can have a contribution from the probe itself.

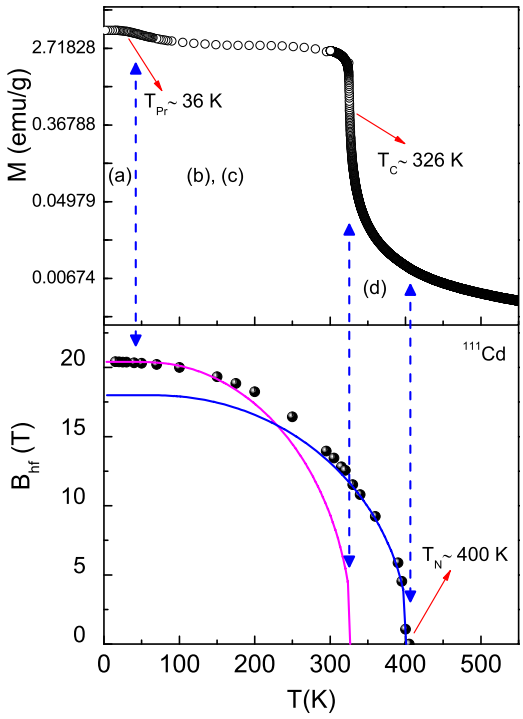


FIG. 3. Magnetization (top) and $B_{hf}$ at $^{111}$Cd probe substituting Mn positions (bottom), for a wide range of temperatures. Magnetization measurements reveal multimagnetic transitions. The $B_{hf}$ obtained by PAC spectroscopy shows smooth changes in the regions that correspond to magnetic transitions. Regions (a), (b), (c), and (d) indicate different magnetic phases observed by magnetization and correspond to different magnetic structures as displayed in Fig. 4.

The magnetic measurements using H = 100 Oe (top of Fig. 3) show several magnetic transitions with good resolution. One can observe the first transition from paramagnetic to antiferromagnetic phase. This transition is also clearly observed in the PAC measurements. The second transition from antiferromagnetic to ferromagnetic phase is seen more clearly in magnetization measurements from which $T_C$ = 326.2 K was determined. The third transition is a small contribution corresponding to the Pr-4f spin sublattice ordering approximately at $T_{Pr}$ = 36 K and was observed only in magnetization measurement. This transition contributes to a slight increase in the magnetization as shown in Fig. 3. The regions (a), (b), (c) and (d) in the Fig. 3 indicate different magnetic phases presented in this compound as established by neutron diffraction measurements[4] and whose magnetic structures are shown in Fig. 4.

Fig. 4 displays, for a better comprehension, a schematic presentation taken from the neutron diffraction study of Welter et. al.[4] for $PrMn_2Ge_2$ in which the structures of each magnetic ordering are shown with directions of Mn and Pr spins. Some of these phase transitions were identified in the PAC and magnetization measurements. For example, above 400.3 K we have pure paramagnetic phase. Below 400.3 K, the canted structure with antiferromagnetic ordering (AFl) appears followed by the ferromagnetic phase (Fmc) at about 326.2 K due to spin reorientation along the c-axis. At about 142 K the conical ferromagnetic structure (Fmi) appears in the Mn layers. This phase transition however, is not observed in the PAC or magnetization measurement. At about 36 K the Pr spin ordering starts. According to Welter et. al. however, the Pr spins sublattice orders only in the presence of an external field.[4] This phase transition is clearly observed in the magnetic measurements with H = 100 Oe but not in PAC data.

The contribution of Pr spin ordering could not be observed in the PAC measurements with $^{111}$ Cd probe. However, analyzing the values of the magnetic hyperfine field, in the saturation region, measured with PAC spectroscopy using $^{111}$Cd probe nuclei in compounds $RMn_2Ge_2$, with R = La, Ce, Nd of the same family of $PrMn_2Ge_2$ (see Table I), one can observe that, although these values are quite close to each other, $B_{hf}$ slightly increases from R = La to R = Pr, following the decrease in the distance

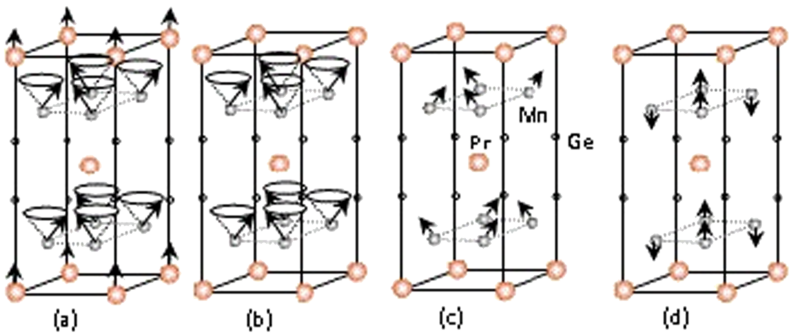


FIG. 4. Magnetic structure for different phases in $PrMn_2Ge_2$. (d) Below 400.3 K, Mn atoms orders antiferromagnetically (AFl) followed by a (c) canted ferromagnetic phase (Fmc) at about 326.2 K due to Mn spin reorientation along the c-axis, which changes to a (b) conical ferromagnetic structure (Fmi) at about 142 K. (a) Pr spin ordering starts at about 36 K. For more details see Welter et. al.[4]

TABLE I. Values of $B_{hf}$(T), $T_C$(K) and $T_N$(K) measured with $^{111}$Cd in $RMn_2Ge_2$ (R = La, Ce, Pr and Nd). The distance between two nearest neighbor Mn atoms, $d_{Mn\text{-}Mn}$ is also displayed for these compounds.

| Sample | $B_{hf}$(T) (T) | $T_N$(K) (K) | $d_{Mn\text{-}Mn}$ Å | reference |
|---|---|---|---|---|
| $LaMn_2Ge_2$ | 19.6(2) | 418.0(1) | 2.965(1) | 8 |
| $CeMn_2Ge_2$ | 20.3(1) | 408.0(2) | 2.920 | 14 and 17 |
| $PrMn_2Ge_2$ | 20.4(1) | 400.3(1) | 2.917(1) | This paper |
| $NdMn_2Ge_2$ | 20.0(1) | 419.8(1) | 2.898(1) | 16 |

between Mn atoms ($d_{Mn\text{-}Mn}$) in these compounds, as expected. Table I also shows that $T_N$ decreases for the same sequence of compounds. This shows some kind of correlation between the hyperfine field and $d_{Mn\text{-}Mn}$ and $T_N$. The exception to this behavior is $NdMn_2Ge_2$ to which, although $d_{Mn\text{-}Mn}$ follow the systematics of the $RMn_2Ge_2$ family, $B_{hf}$ does not. $T_N$ also goes to the opposite direction from the rest of the family with an increase from $PrMn_2Ge_2$ value. This change is an indication that the exchange interaction between Mn-Mn ions in $NdMn_2Ge_2$ may be different from the other three compounds with an influence on $B_{hf}$. The results given in Table I also suggest that the ordering of Pr spins sublattice is not observed by $^{111}$Cd probe. Same conclusion was reached in the PAC study of $NdMn_2Si_2$ compound.[16] Thus, probably the $^{111}$Cd probe is more sensitive to the $d_{Mn\text{-}Mn}$ distance in the intra-layer rather than the $d_{Mn\text{-}Pr}$ distance in the inter-layer due to its location.

## IV. SUMMARY

The X-ray diffraction results showed that the samples crystallize in the $ThCr_2Si_2$ with $I4/mmm$ space group confirming the result of the previous study.[11] The temperature dependence of of $B_{hf}$ at Mn sites determined from the PAC measurements in $PrMn_2Ge_2$ compounds using $^{111}$Cd probe nuclei showed the expected behavior with a transition from paramagnetic to antiferromagnetic and then to ferromagnetic order and allowed the determination of $T_N$ with accuracy. The transition temperature ($T_C$) for the antiferromagnetic to ferromagnetic phase could not be defined with the same accuracy. Magnetization measurements show clear transitions from paramagnetic to antiferromagnetic then to ferromagnetic order. Moreover, magnetization measurements showed the Pr spin ordering that PAC measurement with $^{111}$Cd did not reveal, reinforcing the suggestion that the $^{111}$Cd probe nuclei substituting Mn position in this compound are not sensitive enough to Pr sublattice ordering. The ferromagnetic ordering along c-axis with conical ferromagnetic structure (Fmi) in the Mn layers suggested in some earlier work was not observed in this work suggesting that this transition is quite soft to be identified with these technique.

## ACKNOWLEDGMENTS

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