Study of the effect of disorder on the local magnetism in Heusler alloys

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A local study of the influence of annealing temperature that can provoke structural defects and chemical disorder on the magnetism of Heusler alloys has been carried out by measuring hyperfine interactions in Pd_2MnZ (Z=Ge, In, Sn, and Sb). Perturbed angular correlation method has been used to measure the hyperfine fields at ^{111}Cd probe nuclei substituting the Mn and Z sites as a function of temperature. The fraction of ^{111}In-nuclei-occupying Mn sites was found to increase with the annealing of sample at higher temperatures followed by quenching that can leave the alloy in a disordered state. As a consequence, it was possible to observe the effect of temperature in the ordering of the alloys. Moreover, electric quadrupole interaction measurements clearly indicated chemical disorder after quenching in Pd_2MnSn and an improvement in the ordering of the Pd_2MnGe structure at high temperatures. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2172222]

I. INTRODUCTION

Heusler alloys are one of the most important model systems in the study of magnetism due to the possibility to investigate different magnetic phenomena in the same family of alloys. An interesting feature of these alloys is that the magnetic order is strongly dependent upon the state of the chemical order. The X_2YZ Heusler alloys have a cubic $L2_1$ structure consisting of four fcc sublattices, and if one of the X sublattices is unoccupied, the resulting alloy with $C1_b$ structure is called half-Heusler alloy. The potential for technological application of Heusler alloys has enormously increased recently since it was shown that some Heusler alloys (either half or full) are half metal, where the minority band is semiconducting with a gap at the Fermi level which leads to a full spin polarization. This characteristic makes such alloys good candidates for application in spintronics and spin injection. It was pointed out that disorder in full Heusler alloys could degrade the half metallicity of these Heusler alloys.[1–3] A local study of the influence of disorder on the magnetism of Heusler alloys is therefore highly desirable. The present work reports the measurement of the magnetic hyperfine field (mhf) at Y and Z atomic sites in full Heusler alloys Pd_2MnZ (Z=Ge, In, Sn, and Sb) as a function of annealing temperature, since the annealing procedure can provoke disorder in these alloys. When Z=Ge, Sn, and Sb the alloys present ferromagnetic order with Curie temperatures of 170, 189, and 247 K, respectively. The alloy Pd_2MnIn on the other hand orders antiferromagnetically below 142 K.

II. EXPERIMENTAL PROCEDURE

Heusler alloy samples were prepared by arc-melting the stoichiometric amounts of the constituent elements (99.99% purity) in argon atmosphere purified with a hot titanium getterer. After annealing at 800 °C for 24 h in the argon atmosphere the samples were analyzed by x-ray powder diffraction and were found to be essentially single phase with the correct $L2_1$ structure. The ^{111}In nuclei were implanted in the samples by means of nuclear reactions ^{108}Pd(^{7}Li,$4n$)^{111}In or ^{108}Pd(^{6}Li,$3n$)^{111}In, with a beam energy of 32 MeV using an 8 UD Pelletron Tandem Accelerator. Since Pd is a constituent element of the alloys in the present experiment, the samples themselves served as the reaction targets during irradiation, and practically all the ^{111}In nuclei produced in the reaction stopped in the sample.[4]

Measurements were carried out using a perturbed angular correlation (PAC) spectrometer consisting of four conical BaF_2 detectors with a conventional fast-slow coincidence electronic setup. The gamma cascade of 172–245 keV, populated from the electron capture decay of ^{111}In and having an intermediate level at 245 keV with spin $I=5/2^+$ and $T_{1/2}$=85 ns, in ^{111}Cd was used to measure the hyperfine interaction. The samples were measured in the temperature range of 10–295 K using a closed-cycle helium cryogenic device. The time resolution of the system was about 600 ps.

The PAC method is based on the observation of hyperfine interaction of nuclear moments with extra nuclear magnetic-field or electric-field gradient (efg). A description of the method as well as details about the PAC measurements can be found elsewhere.[5,6] The perturbation factor $G_{22}(t)$ of the correlation function contains detailed information about the hyperfine interaction. Measurement of $G_{22}(t)$ allows the determination of the Larmor frequency $\omega_L=\mu_N g B_{\mathrm{hf}}/\hbar$, the nuclear quadrupole frequency $\nu_Q=eQV_{zz}/h$, as well as the asymmetry parameter $\eta=(V_{xx}-V_{yy})/V_{zz}$, where V_{xx}, V_{yy}, and V_{zz} are the components of the efg tensor in its principal axis system. Consequently, from the known g factor and quadrupole moment Q of the 245 keV state of ^{111}Cd the magnetic hyperfine field B_{hf} and the major efg component V_{zz} can be obtained.

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III. RESULTS AND DISCUSSION

After implantation, before starting the PAC measurements, samples were annealed at 400 °C in vacuum for about 4 h to eliminate the effects of radiation damage. The measurements above the magnetic ordering temperature showed a low-frequency electric quadrupole interaction, which provokes a slight attenuation of the amplitude in the spectra measured below the ordering temperature, but does not interfere in the determination of magnetic hyperfine frequencies. This electric interaction is probably due to some impurities or defects in the crystal structure including chemical disorder.

The results show two distinct magnetic interactions at all temperatures below T_C for the ferromagnetic alloys. For Pd_2MnSn the characteristic Larmor frequencies measured at 10 K were found to be 319 Mrad/s for the component with major fraction (~80%) and 119 Mrad/s for the minor fraction (~20%). The corresponding hyperfine fields (B_{hf}) are 21.2(1) and 7.9(1) T, respectively. The higher-frequency component was assigned to probe nuclei-occupying Sn site and the lower-frequency component to the Mn site in conformity with previous results from *ab initio* calculations.[7] The PAC spectra for the Pd_2MnSb and Pd_2MnGe alloys were analyzed in a similar manner. The Larmor frequencies measured at 20 K, corresponding to major and minor fractions, respectively, are 350 and 317 Mrad/s for Pd_2MnSb and 398 and 291 Mrad/s for Pd_2MnGe. For both alloys the major and minor fractions were found to be ~75% and ~25%, respectively. These results were assigned to Sb/Ge and Mn sites, respectively, corresponding to hyperfine fields of 23.8(2) and 21.6(2) T for Pd_2MnSb and 27.2(3) and 19.8(5) T for Pd_2MnGe. The values of the hyperfine fields are in good agreement with those obtained in the previous studies.[8,9] The temperature dependence of hyperfine fields at both Mn and Z sites for the ferromagnetic Pd_2MnZ is shown in the left column of Fig. 1. In the right column of this figure the reduced mhf as a function of T/T_C is shown to follow quite well the corresponding Brillouin function (lines) for a $J=5/2$ magnetic system.

After an additional annealing of the samples at 800 °C for 24 h in argon followed by a cooling to room temperature within about 15 min, the site occupation showed significant increase in the fraction of Mn site for Pd_2MnSn and Pd_2MnSb alloys. The fractions, respectively, increase from 20% to 57% and from 25% to 35%. This effect was better observed as a pronounced increase in the amplitude of the peaks corresponding to the Larmor frequencies at Mn sites in the frequency spectra for temperatures below T_C before and after the additional annealing at 800 °C for Pd_2MnSn.

As expected the ordered Pd_2MnIn alloy did not show magnetic interaction. This is due to the fact that ^{111}In nuclei are substituting some of the In atoms in this alloy and the crystal structure of the alloy is such that the In site is in between the two layers of Mn atoms having opposite spins. Due to opposing spins of Mn atoms there is no net transfer of spin density to the probe resulting in zero hyperfine field at In site. After an additional annealing of the sample at 800 °C for 12 h followed by a quenching, a unique Larmor frequency with a strong temperature dependence was observed for PAC measurements at low temperatures in this alloy corresponding to a site occupation of ~85%. This frequency was assigned to ^{111}In probe nuclei occupying the Mn sites as a result of chemical disorder, and the value obtained at 20 K is 137 Mrad/s that corresponds to a mhf of 9.4(1) T. The temperature dependence of the mhf measured at low temperatures is shown in Fig. 2 along with the Brillouin curve ($J=5/2$) that matches the experimental data and corresponds to a ordering temperature of ~100 K. It has been reported in

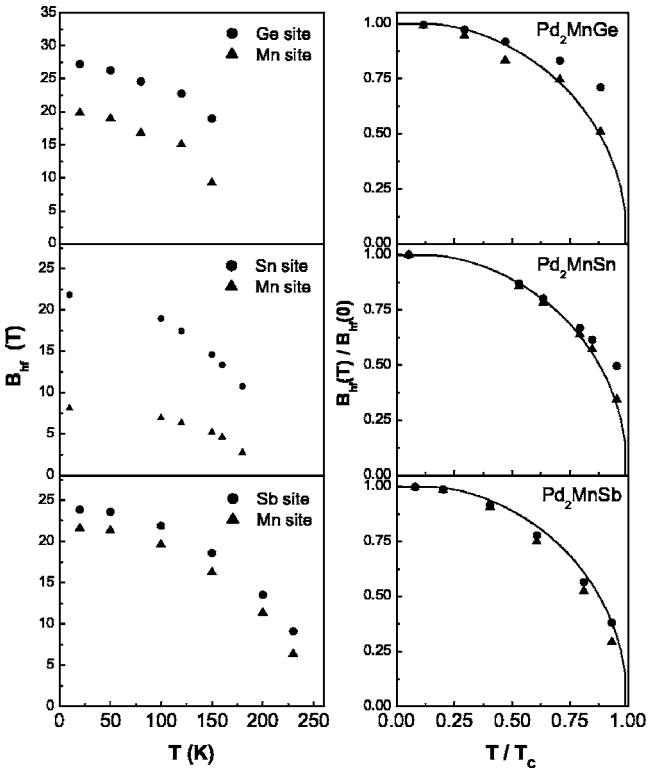

FIG. 1. Temperature dependence of magnetic hyperfine fields in Pd_2MnZ as a function of temperature (left), and corresponding reduced B_{hf} as a function of T/T_C (right). The lines correspond to the $J=5/2$ Brillouin function.

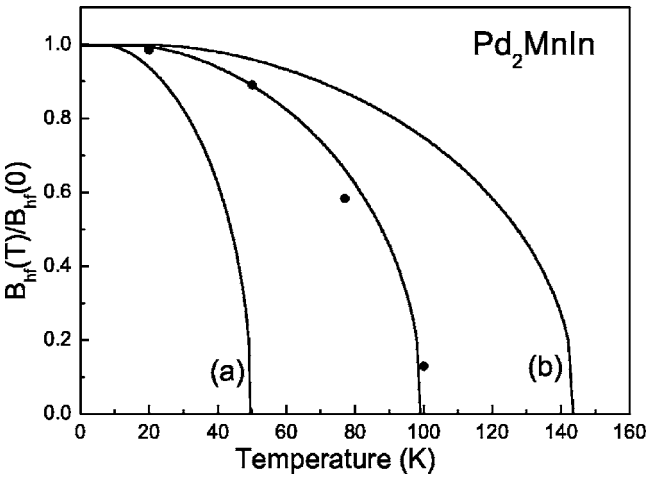

FIG. 2. Temperature dependence of B_{hf} measured at Mn sites in disordered Pd_2MnIn alloy with the corresponding Brillouin function. It also shows the Brillouin curves corresponding to (a) a highly disordered alloy (fast quenched) and (b) ordered alloy (slow cooling) as reported in Ref. 10.

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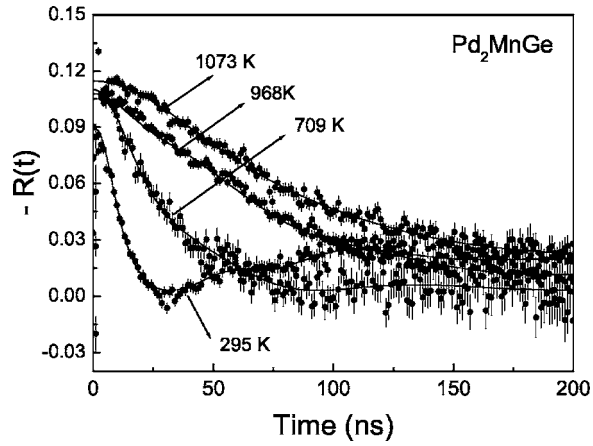

FIG. 3. The perturbation functions for ^{111}Cd probes in Pd_2MnGe at some temperatures above the magnetic ordering temperature.

previous works that the chemical order in Pd_2MnIn depends on the annealing procedure.[10,11] As reported in Ref. 10 after an annealing followed by a fast quenching, the alloy ordered below 50 K. The Brillouin curve corresponding to such ordering temperature as well as that for the ordered alloy are also shown in Fig. 2. From the figure, one can clearly observe that the ordering of this alloys is extremely sensitive to the rate at which the temperature decreases after annealing.

In order to investigate the temperature effect in the ordering process it is necessary to measure the electric quadrupole interaction, which is very sensitive to the ion position around the probe site, at high temperatures. The result for Pd_2MnGe, an alloy particularly hard to obtain free of structural defects, is shown in Fig. 3.

It is clearly seen that the higher the annealing temperature the more ordered is the structure. Figure 4 shows the effect of annealing process on the quadrupole interaction at the probe sites measured at 295 K in Pd_2MnSn. The top part of the figure shows the perturbation function that corresponds to the electric quadrupole interaction spectrum for the sample after the annealing followed by slow cooling. It can be observed that the sample is well ordered with very small structural defects. The ideal function for a cubic system is a straight line parallel to x axis showing no perturbation. In the bottom of the figure the electric quadrupole interaction after an additional annealing followed by quenching is shown. One can observe the presence of a second frequency with $\nu_Q = 150.5(2)$ MHz indicating a disordered environment of a fraction ($\sim 10\%$) of the probe nuclei.

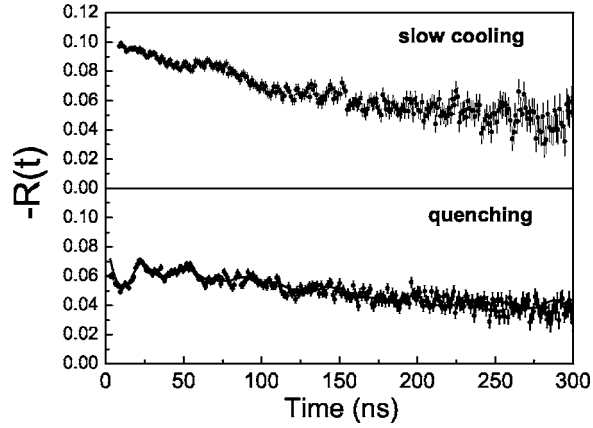

FIG. 4. The perturbation functions for ^{111}Cd probes in Pd_2MnSn at 295 K corresponding to samples with annealing followed by slow cooling (top) and quenching (bottom).

In an ordered cubic alloy, the first next nearest neighbors of either Mn or Sn sites are eight Pd ions, and the second next nearest neighbors of the Mn(or Sn) site are six Sn (or Mn) ions. Therefore, for ^{111}Cd nuclei occupying either Sn or Mn sites in an ordered system a null efg would be observed. However, if there is Sn–Mn disorder a small fraction of probe nuclei in Sn sites for instance would sense a nonzero efg due to the presence of a Mn ion in a Sn site in the second nearest neighborhood of the probes.

IV. SUMMARY

In the present work, besides reporting an efficient method to simultaneously measure the local magnetic field at different sites in magnetic Heusler alloys, it was also shown that the method is sensitive to order/disorder effects that can influence the final site location of the probe. The results of the measurements carried out at different temperatures below the ordering temperature showed two distinct hyperfine fields for the ferromagnetic alloys and no interaction for Pd_2MnIn. The mhf's were assigned to probes substituting the Mn and Z atoms in the ferromagnetic alloys. The population of the probes at Z sites was found to be higher in both cases. After additional annealing at higher temperature, the site occupation showed a significant increase in the fraction of probes at Mn sites. In the antiferromagnetic Pd_2MnIn alloy, where the mhf at In sites is nonexistent from symmetry considerations, it was possible to observe a magnetic interaction due to mhf at Mn site.

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[1] S. C. Lee, T. D. Lee, P. Blaha, and K. Schwartz, J. Appl. Phys. **97**, 10C307 (2005).
[2] S. Picozzi, A. Continenza, and A. J. Freeman, Phys. Rev. B **69**, 094423 (2004).
[3] Y. Miura, K. Nagao, and M. Shirai, Phys. Rev. B **69**, 144413 (2004).
[4] M. N. Rao *et al.*, Braz. J. Phys. **33**, 291 (2003).
[5] W. Pendl, Jr., R. N. Saxena, A. W. Carbonari, J. Mestnik-Filho, and J. Schaft, J. Phys.: Condens. Matter **8**, 11317 (1996).
[6] R. N. Attili, R. N. Saxena, A. W. Carbonari, J. Mestnik-Filho, M. Uhrmacher, and K. P. Lieb, Phys. Rev. B **58**, 2563 (1998).
[7] A. W. Carbonari and H. Haas, Hyperfine Interact. **133**, 71 (2001).
[8] J. Schaf, E. R. Fraga, and F. C. Zawislak, J. Magn. Magn. Mater. **8**, 297 (1978).
[9] J. Schaf, A. F. Pasquevich, W. H. Schreiner, C. C. M. Campbell, E. R. Fraga, and F. C. Zawislak, J. Magn. Magn. Mater. **21**, 24 (1980).
[10] C. M. Hurd, I. Shiozaki, and S. P. McAlister, Phys. Rev. B **26**, 701 (1982).
[11] D. J. Doherty, J. Crangfe, K.-U. Neumann, J. G. Smith, N. K. Zaycr, and K. R. A. Ziebeck, J. Magn. Magn. Mater. **140–144**, 189 (1995).

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