Angle-Dependent Magneto-Resistance near the Pre-Martensitic Phase of Ni$_2$MnGa

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Abstract. Angle-dependent magneto-resistance measurements in the vicinity of the pre-martensite phase ($T_{PM} \sim 219$ K) in Ni$_2$MnGa are reported. Magneto-resistance measurements detect a change in slope, from positive to negative near $T_{PM}$ that can be suppressed with a modest magnetic field. Mirroring this change in slope, published ARPES data [Opeil et al., Phys. Rev. Lett. 100, 165703 (2008)] show a significant depletion of states (pseudo-gap) forming at 0.3 eV below the Fermi energy.

1. Introduction
Ferromagnetic shape-memory alloys based on the Heusler structure are the focus of much applied research owing to their technological importance [1, 2]. In Ni$_2$MnGa the magnetic moment is localized on Mn sites with no moment on Ni sites. Its magnetic character results from the exclusion of minority-spin electrons from Mn-$3d$ states due to strong interactions with Ni $d$ states. Since the Mn-Mn distance is large ($\leq 4$ Å), an indirect Ruderman-Kittel(RK)-type indirect exchange interaction gives rise to magnetism in this material [3, 4]. At room temperature Ni$_2$MnGa is ferromagnetic, and has the L21 Heusler structure (Fm3m). Its Curie point is $T_C = 381$ K, and undergoes a martensitic transition at $T_M \sim 194$ K. Prior to $T_M$, a pre-martensitic phase occurs ($T_{PM} \sim 195$-235 K) that has been the subject of much theoretical and experimental investigation over the last decade [5, 6, 7, 8, 9, 10]. This intermediate phase is described by a Landau-type model where a weakly first-order transition originates from a magneto-elastic coupling between magnetization and the anomalous softening of the TA$_2$ [110] phonon branch. This branch is also implicated in a Fermi-surface reconstruction [11, 12]. Similar electron-phonon coupling and Fermi surface-nesting features are found to be responsible for the pre-martensite behaviors of NiAl and NiTi alloys [13, 14].

Previous magneto-resistance experiments on thin-film and polycrystal Ni$_2$MnGa indicate a large negative magneto-resistance [15, 16, 17]. Evidence for positive-to-negative switching in the pre-martensite phase is understood to be an interplay of Zeeman energy, twin-boundary motion, and a high magneto-crystalline anisotropy. Subsequent magneto-resistance experiments on polycrystal Ni$_{1.75}$Mn$_{1.25}$Ga with a low martensite transition temperature, $T_M = 76$ K [18]
show no evidence of positive-to-negative switching in the pre-martensite phase but a complete switch from a negative (-0.175 %/T at 150 K) to a positive (+0.0375 %/T at 100 K) change in magneto-resistance in the austenite phase. The negative magneto-resistance behavior is understood to originate from an s-d scattering model [19]. The applied magnetic field reduces the s-conduction electron scattering by localized d spins, increasing the mean time between collisions and produces a negative slope in the magneto-resistance with magnetic field. At 50 K the magneto-resistance is again negative in character, but with a different field dependence noted at higher temperature. In contrast to previous experiments we are motivated to understand the changes in magneto-resistance that occur in the pre-martensite phase and their relationship to the significant depletion of states shown by previous ultra-violet photoemission spectroscopy at 0.3 eV below the Fermi energy [20] and the Fermi surface nesting predicted by Lee et al. [12].

2. Experiment
A large single crystal of Ni$_2$MnGa alloy was grown in a sealed quartz tube by the Bridgman technique. Samples were spark cut from this well-characterized single crystal [20], and resistivity measurements were made with a Quantum Design physical properties measurement system (PPMS) using a four-point probe ac technique. The sample was mounted with GE varnish and oriented with the magnetic field perpendicular to the [001] surface.

3. Results and Discussion
Figure 1 shows clear signatures of both a pre-martensitic phase transition (PMT) and a martensitic phase transition (MT) in resistivity. The PMT is indicated by the slight depression of resistivity in the monotonic cooling curve and extends over a broad region 197 < T < 235 K. The PMT feature has no measurable hysteresis associated with this region and agrees with previous measurements for a polycrystal sample of the same composition [16]. In contrast, the MT at ~196 K is a sharply defined first-order transition. The insert to Figure 1 shows $d\rho/dT$ as a function of temperature and illustrates a thermal hysteresis of ~7.4 K.
Figure 2. (a) Isothermal magneto-resistance of Ni$_2$MnGa as a function of applied magnetic field at temperatures indicated to the right. Between each temperature measurement the sample was heated to 300 K and cooled in zero field. (b) The percent change of isothermal magneto-resistance versus applied magnetic field for Ni$_2$MnGa. Results are symmetric about the vertical axis, for clarity only select temperatures and positive values of field are plotted. Solid lines are a guide to the eye.

In order to probe the connection between charge and spin we performed isothermal magneto-resistance at intervals of 2.5 K throughout the premartensite and martensite phase transition $190 < T < 235$ K. Between each measurement we cycled the sample to room temperature then down to the next temperature interval in zero field to assure magnetic domain relaxation. Figure 2a shows that at 235 K and 190 K the magneto-resistance of Ni$_2$MnGa has a negative slope as the applied field is increased from 0 to $\sim 0.5$ T, however, as $T$ approaches $T_{PM}$ ($\sim 217.5$ K) another scattering regime develops between $s$ conduction electrons and $d$-state electron spins leading towards a change in the magnetic response of the material. The magnetic scattering regime is indicated by switching from a positive to negative slope in the magneto-resistance as magnetic field reaches 0.5 T. At temperatures slightly above and below $T_{PM}$ this new scattering regime is suppressed by increasing the magnetic field. Figure 2b illustrates the percent change of isothermal magneto-resistance versus applied magnetic field as temperature is reduced from 235 to 190 K. Although our results are symmetric about the vertical axis, only select temperatures and positive values of field are plotted. The largest positive change of $+1.4 \%/T$ is indicated at 217.5 K, while for temperatures at the extremes of the premartensite phase (235 K, 190 K) Ni$_2$MnGa demonstrates a monotonic negative magneto-resistance of about $-0.3 \%/T$.

We conclude that the switching from positive to negative magneto-resistance in Ni$_2$MnGa results from a shift in valence Mn and Ni $d$-band electrons and an associated pseudo-gap onset when approaching the martensite transition as illustrated by previous UV photoemission spectroscopy [20]. The first-principles electronic structure calculations associated with the pseudo-gap formation confirm the shift in both Mn and Ni-$d$-states and nesting of the Fermi surface. Because the local magnetism of this system relies on the strong interaction of Mn 3$d$ states and Ni-atom $d$ states, one expects a deviation of magnetic behavior as the pseudo-gap is approached that relies on a redistribution of Mn and Ni $d$ states. The application of a magnetic field in excess of $\sim 0.5$ T raises the electrons to a sufficient energy allowing a redistribution of $d$ states similar to what existed prior to the onset of the pseudo-gap formation and thus
the resumption of a negative slope in magneto-resistance. We note that our explanation of magneto-resistance at pre-martensite temperatures is in contrast to the one given by Biswas and coworkers [16], which relies on the interplay of Zeeman energy, twin boundary motion and a high magneto-crystalline anisotropy.

References
[1] A. Chakrabarti et al., Phys. Rev. B 72, 073103 (2005).
[2] Z. D. Han et al., Solid State Comm. 146, 124 (2008).
[3] J. Kubler, A. R. Williams, and C. B. Sommers, Phys. Rev. B 28, 1745 (1983).
[4] S. R. Barman, S. Banik, and A. Chakrabarti, Phys. Rev. B 72, 184410 (2005).
[5] A. Planes et al., Phys. Rev. Lett. 79, 3926 (1997).
[6] A. Chernenko et al., Phys. Rev. B 57, 2659 (1998).
[7] Alfons Gonzalez-Comas et al., Phys. Rev. B 60, 7085 (1999).
[8] L. Manosa et al., Mater. Sci. and Engr. A273-275, 329 (1999).
[9] J. Wan et al., Phys. Lett. A 327, 216 (2004).
[10] V. A. Chernenko et al., Scripta Mater. 55, 303 (2006).
[11] L. Manosa et al., Phys. Rev. B 55, 11068 (1997).
[12] Y. Lee, J. Y. Rhee and B. N. Harmon, Phys. Rev. B 66, 054424 (2002).
[13] G. L. Zhao and B. N. Harmon, Phys. Rev. B 45, 2818 (1992).
[14] G. L. Zhao and B. N. Harmon, Phys. Rev. B 48, 2031 (1993).
[15] V. O. Golub et al., J.Appl. Phys. 96, 3865 (2004).
[16] C. Biswas, R. Rawat and S. R. Barman, Appl. Phys. Lett. 86, 202508 (2005).
[17] I. Yu et al., Mater. Sci. Eng. A 481-482, 651 (2008).
[18] S. Banik et al., Phys. Rev. B 77, 224417 (2008).
[19] M. Kataoka, Phys. Rev. B 63, 134435 (2001).
[20] C. P. Opeil et al., Phys. Rev. Lett. 100, 165703 (2008).