Calorimetry of Ferromagnetic Heuslers in Magnetic Fields: Observation of a Pseudo-gap in a Ni$_2$MnGa Single Crystal


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Work sponsored by: Dept. of Energy and Boston College
Ni$_2$MnGa Single Crystal

Low Energy Electron Diffraction (LEED) at T=293 K

Ni$_2$MnGa (100) Cubic Fm-3m a = 5.825 Ang. Vol = 192.34 Ang.$^3$ Ni (0.25,0.25,0.25) Mn (0.5,0.5,0.5) Ga (0, 0, 0)
Curie Temp. Transition:

$T_C$ - $\rightarrow$ Ferromagnetic Transition

Dilatometry
Martensite and Pre-martensite Temperatures

$T_C$ is field independent
FCC to Monoclinic at MT

MT is field independent
FCC to Monoclinic at MT

$T_C$: 385 K

MT: 197 K

PMT: 214 K
Specific Heat \((H = 0 \text{ g})\)

\[ C/T = \gamma + B_3 T^2 \]

\(T_{\text{range}} = 2 - 30 \text{ K}\)

\[ \gamma = 10.0 \]

\[ B_3 = 0.2123 \]

\[ \Theta_D = 332 \text{ K} \]
Specific Heat \((H = 90,000 \text{ g})\)

\[ T_{range} = 2 - 30 \text{ K} \]

\[ C/T = \gamma + B_3 T^2 \]

**Ni₂MnGa**

90,000 G

- \( \gamma = 9.7 \)
- \( B_3 = 0.2131 \)
- \( \Theta_D = 330 \text{ K} \)
Specific Heat: Global Data \((H = 0 \text{ to } 90,000 \text{ g})\)

\(\text{Ni}_2\text{MnGa}\)

[global: \(B = 0 \text{ to } 90,000 \text{G}\)]

\[
\frac{C}{T} = \gamma + B_3 T^2
\]

\[
\gamma = 10.1
\]

\[
B_3 = 0.2172
\]

\[
\Theta_D = 330 \text{ K}
\]
Specific Heat Analysis of Ni$_2$MnGa:

\[
\frac{C}{T} = \gamma + B_3T^2
\]

\[
T_{\text{range}} = 2 - 30 \text{ K}
\]

<table>
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<th>B(G)</th>
<th>$\gamma$ (mJ K$^{-2}$ mol$^{-1}$)</th>
<th>$B_3$ (mJ K$^{-4}$ mol$^{-1}$)</th>
<th>$\Theta_D$ (K)</th>
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Normative for Magnetic Materials

Comparable to Cu
Specific Heat  \( T = 2 - 300 \text{ K}, B = 0 \) to \( 90000 \text{ g} \)

![Graph showing specific heat of Ni₂MnGa with various magnetic fields and the Curie temperature \( T_M = 202 \text{ K} \).]
Specific Heat $T = 2 - 300$ K, $B = 0$ g

Ni$_2$MnGa

$B = 0$

$C$ (J K$^{-1}$ mol$^{-1}$) vs $T$ (K)

- $C_D$ [$\Theta_D = 325$ K ($\rho_D = 10.5$)]
- $C_{E1}$ [$T_{E1} = 1500$ K ($\rho_{E1} = 1.5$)]
- $C_e$ [$\gamma = 10.1$ mJ K$^2$ mol$^{-1}$]
- $C_{calc}$
Specific Heat \( T = 2 - 300 \text{ K}, \ B = 10000 \text{ g} \)

![Graph showing specific heat of \( \text{Ni}_2\text{MnGa} \) at 10,000 G. The graph plots specific heat \( C \) in \( \text{J K}^{-1} \text{ mol}^{-1} \) against temperature \( T \) in K. The graph includes various lines and markers indicating contributions from different processes, such as phonon 
(\( C_D \), with Debye temperature \( \Theta_D = 325 \text{ K} \)), electron 
(\( C_e \), with \( \gamma = 10.1 \text{ mJ K}^2 \text{ mol}^{-1} \)), and others. The markers represent experimental data, while the lines represent theoretical or calculated contributions.]
Specific Heat: $C_{\text{Total}} - C_{\text{Lat}} - C_{\text{e}}$

Ni$_2$MnGa

$B = 0$

$\Delta S_M = 5.6 \text{ J K}^{-1} \text{ mol}^{-1}$

$\Delta H_M = 1,030 \text{ J mol}^{-1}$

$\Delta S_L = 0.9 \text{ J K}^{-1} \text{ mol}^{-1}$

$\Delta H_L = 170 \text{ J mol}^{-1}$

Mn Oxide

$magnetic impurity$

$T_M = 200 \text{ K}$

$226K, 237K$
Specific Heat: $C_{\text{total}} - C_{\text{Lat}} - C_{e}$

Ni$_2$MnGa

10,000 G

$\Delta S_{M} = 5.2$ J K$^{-1}$ mol$^{-1}$
$\Delta H_{M} = 970$ J mol$^{-1}$

$\Delta S_{L} = 1.1$ J K$^{-1}$ mol$^{-1}$
$\Delta H_{L} = 200$ J mol$^{-1}$

$T_{M} = 202$ K

magnetic impurity
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<th>$T_M$ (K)</th>
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The average values given in red are probably reasonable estimates for the field-independent parameters.

$\Delta S_M = \text{Entropy Change due to M Transistions}$

$\Delta H_M = \text{Enthalpy Change}$

$\Delta S_L = \text{Entropy Change (Latent) due to PM Transistion}$

$\Delta H_L = \text{Enthalpy Change (Latent)}$
Resistivity (AC Transport)

Rotator puck
04oct07_01
Ni$_2$MnGa single crystal
Resistivity (AC Transport), $\rho(T)$:

Rotator puck
04oct07_01
Ni$_2$MnGa single crystal
ρ(T) (close up):

Rotator puck
04oct07_01
Ni$_2$MnGa single crystal
\( \rho(T) : \)

- Resistivity cooling (Ohm-cm)
- Resistivity warming (Ohm-cm)

Rotator puck
04oct07_01
Ni\(_2\)MnGa single crystal

m-a crystallographic changes
Magneto-Resistivity, $\rho(H, T)$, where $H_{\text{MAX}} = 9$ T:
Magneto-Resistivity, $\rho(H, T)$:

Does the $H$-field couple with spins or charge in the non-monotonic temperature regime?
Magneto-Resistivity, $\rho(H, T)$:

Does the $H$-field couple with spins or charge in the non-monotonic temperature regime?
\( \rho(\mathbf{H}, T): \)

- 298 K
- 265 K
- 220-0 K
- 200 K
$\rho(H, T)$:

![Graph showing resistivity (ohm-cm) vs. H field (T) for different temperatures (220 K, 215 K, 210 K).]
\[ \rho(H, T): \text{Material Coupling with } H\text{-field.} \]
Dilatometry

MT 197 K

MT is field independent

FCC to Monoclinic at MT

PMT 214 K

Fermi Surface Map

FIG. 3. Fermi surfaces for various magnetizations at $k_z = 0.5$. The nesting vector with $\zeta = \frac{1}{3}$ is denoted by the arrow.

Temperature Dependent UV-Spectroscopy ($h\nu=21.21\text{eV}$)

![Temperature Dependent UV-Spectroscopy Graph](image)
Temperature Dependent UV-Spectroscopy \((h\nu=21.21\text{eV})\)
ARPES: Angle Resolved Photoemission Spectroscopy

\[ E_{\text{kinetic}} = h\nu - e\Phi - E_{\text{binding}} \]

\[ k_{\parallel} = \sqrt{\frac{2m_e E_{\text{kinetic}}}{\hbar^2}} \cdot \sin \phi \]

**ARPES** - choose azimuthal \( \theta \) to specify k-vector to probe, and then vary polar \( \phi \) to collect DOS at various \( k_{\parallel} \) and observe dispersion of bands along k-vector.
Energy Dispersion Curves:

FIG. 9: Photoemission spectra at fixed angle, for angles between 0° to 55° in 5° increments. Intensity is plotted versus binding energy in Ni₂MnGa at (a) T = 219 K and (b) 173 K in close proximity to the pre-martensitic transition. The momenta, \( k_\parallel \), are quoted at the Fermi energy for the fcc phase, and vary by about 7% across each spectrum. The black lines superimposed over the photoemission spectra are meant to describe qualitatively the dispersion of the various structures present in these plots.
Evidence of pseudo-gap in KMo$_6$O$_{17}$ (Purple-bronze):

T-dependent photoemission of KMo$_6$O$_{17}$ (purple-bronze) RT to 45 K.

Summary:

1. $T^{3/2}$ behavior not found. No CDW or SDW evident in low T behavior. MT seems H independent. Further investigation on PMT suggests ???

2. The martensite, Ni$_2$MnGa, exhibits a “pseudo-gap” behavior at B.E. $= 0.3$ eV as T $\rightarrow T_{MT}$.

3. Pseudo-gap at PMT appears to be imperfect nesting (dispersion in ARPES) while perfect nesting occurs at the MT (no dispersion in ARPES).

4. The pre-martensite transition is a failed attempt to transition to a lower energy state.


6. Are pseudo-gaps just a generic feature of metals/alloys?
Evidence of pseudo-gaps in other materials:

ARPES at (π,0) for u-doped Bi2212, 90K Pseudo-gap state, 30K-SC state.

T-dependent photoemission of KMo$_6$O$_{17}$ (purple-bronze) RT to 45 K.

Norman et al., Adv. in Physics, 54 (2005)

Evidence of pseudo-gap in Bi$_{2212}$:

ARPES at (π,0) for u-doped Bi$_{2212}$, 90K Pseudo-gap state, 30K-SC state.

Ni$_2$MnGa data

Norman et al., Adv. in Physics, 54 (2005)
Notes:

Above the MT temperature the bands appear to move and accommodate shifts in energy as it is removed from the system.

At the below the MT temperature the energy dispersion bands change little across k//, which suggests that the FS bands are flat and FS nesting is possible. Nesting of the FS bands allows the system to be reduced in energy, by a reduction of the number of states. This reduction in the allowed density of states is indicated by UV-photoemission as a pseudo-gap forming close ($E_B=0.3$ eV) to the $F_E$. 
Slide 1. Thank you for coming to this talk this afternoon. My name is Cyril Opeil and I am from Boston College. Discuss our observation of a pseudo-gap in the Heusler alloy, Ni2MnGa and what this means.

Define pseudo-gap: a shift or change in the density of states in proximity to the Fermi edge.

Many people have worked on this martensite material because they have industrial applications in actuators and magnetic memories. The rationale for this work is to better understand the martensite transition and the pre-martensite transition.

The experimental method to probe this material is photoemission.

I want to begin by acknowledging my colleagues Jason Lashley...

The work is sponsored by DOE and BC.

We see the crystal specimen used in the experiments.

Because I am a Jesuit and priest, I want to put in a word for my other sponsor.

There is some danger in doing photoemission on ferromagnetic materials. Often people have questions related to spin polarized data on these materials. We are looking at the density of states. Spin polarized experiments on this material is the subject of another talk.

Slide 2. In order to do photoemission we need to have a good crystal, here is the room temperature LEED picture indicating long range order of the crystal surface. The surface was prepared by polishing, and then in the spectrometer, Ar sputtering and annealing.

To show that the bulk and surface are both well ordered cubic structures we show the Laue performed on our sample. We note that at room temperature it is cubic material. At the Martensite transition it goes from cubic to monoclinic in crystal structure. Here at the bottom right is the atomic stacking of Ni, Mn and Ga.

Slide 3. This material is well characterized, here we show the magnetic transition from paramagnetic to ferromagnetic ordering. The ordering for our sample starts at 370-380 K and is fully developed at about 275 K.

Heat capacity measurements reveal the first order martensite transition at a little less than 200, the PMT is a bit above 200.

From the data we can calculate the Debye temperature at about 325 K and the Einstein temperature is about 1500 K.

Slide 4. To further characterize the sample we did dilatometry.

We see clearly the PMT, a broad feature of about 15 degrees, centered at 214 K and the field independent MT at about 194 K.

The reason we chose to do photoemission on this martensite is because of a hypothesis raised by Lee in 2002, physical review B. There thought was that the material at the MT undergoes Fermi surface nesting to lower the energy states. The red arrow denotes the direction along nesting may occur.

We thought we might be able to see if this was true is we did temperature dependent photoemission. We took samples of the density of states as temperature is decreased, from room temperature down to 173 K. to check if a pseudo-gap develops.
5. Looking at temperature dependent UV photoemission from 229 to 173 K we see that over this 56 degree interval we note that we have a large density of states change. We note also that not much happens as the temperature is lowered through the PMT. The PMT is a failed attempted at nesting. The conditions of phonon softening, energy and crystal structure are not adequate for nesting to occur. One might think of the PMT as a breather mode that tries to nest but it can not.

6. Let's look at an enlarged version of this slide. We see energy versus intensity of the temperature dependent data. The red trace shows a large density of states at 0.3 eV which shifts significantly as we move through the martensite transition to the black trace. pulling away from the Fermi edge. To confirm our evidence that we are looking at nesting we have to do ARPES and see how the energy dispersion curves as the angle is changed.

7. For those who are not familiar with ARPES. Here is the oriented crystal surface where the analyzer is fixed. We change the angle of the crystal surface, phi. We show our results across the change in phi, which is the tilt angle of the crystal. Energy is along the vertical axis and $K// \square$ is along the bottom of both graphs. $k// \square$ is proportional to the tilt angle. We see that across the temperature range 295-219 K, over the 76 k interval, not much is happening. Note the contour height (intensity) color key at the top, red is the highest, dark blue is lowest intensity.

8. ARPES from 219 to 173K we note a dramatic change is the density of states over $K// \square$ binding Energy is along the vertical axis, $k// \square$ is along the horizontal axis. Finally we see the energy dispersion curves at 219 K and 173 K. We see at the left that there is a great deal of dispersion in the bands as we sweep over phi. This indicates that the Fermi surface fails to nest at the PMT. At the right we see ARPES at 173 K. it exhibits almost no dispersion while scanning phi form 0 to 55 degrees. This confirms that nesting occurs upon the Martensite transition.

9. Other materials exhibit pseudo gaps whose origins are different. I have here examples of Bico 2212 and purple bronze. The reason I compare these data is to show how large the pseudo gap is in the case of the Ni2MnGa.

10. Compare the energy axis for Bisco and Ni2MnGa

11. same as 12 comment.

12. summarize