The Physics Department at Boston College, Higgins Hall
When a Good Martensite Metal... Goes Bad!

C. P. Opeil\textsuperscript{1}, J. C. Lashley\textsuperscript{2}, R. A. Fisher\textsuperscript{3}, R. K. Schulze\textsuperscript{2}, B. Mihaila\textsuperscript{2}, J. L. Smith\textsuperscript{2}, P. Riseborough\textsuperscript{4}, L. Mañosa\textsuperscript{5} and A. Planes\textsuperscript{5}

\textsuperscript{1}Boston College, Physics Department, Chestnut Hill, MA, USA
\textsuperscript{2}Los Alamos National Laboratory, Los Alamos, NM, USA
\textsuperscript{3}Univ. of California, Berkeley-Lawrence/Berkeley Laboratory, CA, USA
\textsuperscript{4}Temple University, Physics Department, Philadelphia, PA, USA
\textsuperscript{5}Universitat de Barcelona, Departament d’Estructura i Constituents de la Matèria, Facultat de Física, Diagonal 647, E-08028 Barcelona, Catalonia, Spain

Work sponsored by: Dept. of Energy and Boston College
Hey George, do you know how a good martensite metal... turns bad?
• Magnetic moment on Mn atoms: \( \mu \approx 4.2 \mu_B \)
• Coupling RKKY
• Ferromagnetic order
• Weak magnetic anisotropy.

**High T:**
Heusler, L2₁ (Fm3m)

**Martensitic Transition****** and related properties

Solid state transition: first-order, diffusionless, driven by shear mechanisms.

Shape-Memory effect

CUBIC PHASE

(a) $T > A_f$

MARTENSITE

(b) $T < M_s$

(c) $T < M_f$

Strain
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)

Back Scatter Laue, T = 293K

Los Alamos National Laboratory
The World’s Greatest Science Protecting America
\( \rho(T) \) (close up):

Rotator puck
04oct07_01
Ni\textsubscript{2}MnGa single crystal
\[ \rho(T) : \]

Graph showing the resistivity cooling and warming of a \( \text{Ni}_2\text{MnGa} \) single crystal as a function of temperature. The graph highlights the martensite crystallographic changes at specific temperatures. The data is labeled as 'Rotator puck 04oct07_01'.
Abe, what’s this? Is our martensite metal good or is it… going bad?

\[ \rho(T) : \]

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

Martensite crystallographic changes

Rotator puck
04oct07_01
Ni$_2$MnGa single crystal
"This could be the discovery of the century. Depending, of course, on how far down it goes."
"This could be the discovery of the century. Depending, of course, on how far down it goes."
Resistivity? Well, what the heck is resistivity?
Resistance and Resistivity: Electrical Transport
Resistance and Resistivity: Electrical Transport
Resistance and Resistivity: Electrical Transport

Resistance \( R \) [ohms] = \( V \) [volts] / \( i \) [amps]

Ohm’s Law
Resistance and Resistivity: Electrical Transport

Resistance: \[ R_{\text{ohms}} = \frac{V_{\text{volts}}}{i_{\text{amps}}} \]

Resistivity: \[ \rho_{\text{ohms-cm}} = \frac{R_{\text{ohms}} \times A_{\text{cm-cm}}}{d_{\text{cm}}} \]
Resistance and Resistivity: Electrical Transport

Resistance
\[ R \text{ [ohms]} = \frac{V \text{ [volts]}}{i \text{ [amps]}}, \]

Resistivity
\[ \rho \text{ [ohms-cm]} = \frac{R \text{ [ohms]} \times A \text{ [cm-cm]}}{d \text{ [cm]}}, \]
\[ \rho \text{ [ohms-cm]} = \frac{V \text{ [volts]} \times A \text{ [cm-cm]}}{i \text{ [amps]} \times d \text{ [cm]}}. \]
Resistance and Resistivity: Electrical Transport

Resistance

\[ R \text{ [ohms]} = \frac{V \text{ [volts]}}{i \text{ [amps]}}, \]

Ohm’s Law

Resistivity

\[ \rho \text{ [ohms-cm]} = \frac{R \text{ [ohms]} \times A \text{ [cm-cm]}}{d \text{ [cm]}}, \]

\[ \rho \text{ [ohms-cm]} = \frac{V \text{ [volts]} \times A \text{ [cm-cm]}}{i \text{ [amps]} \times d \text{ [cm]}}, \]

\[ \rho (T) = \frac{V \times A}{i \times d}, \]

normal metallic behavior

Temperature (K)
Resistivity (AC Transport)

\[ \text{Resistivity cooling (Ohm-cm)} \quad \text{Resistivity warming (Ohm-cm)} \]

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

- Non-monotonic behavior
- Sudden energy shifts

Graph showing Resistivity cooling (Ohm-cm) and Resistivity warming (Ohm-cm) for a Rotator puck.

Ni$_2$MnGa single crystal
Pre-Martensite Transition Resistivity (H = 0 T):

Scales offset (7x10^{-6}) for comparison

7.40 K
Magneto-resistance ($H = \pm 1$ to $-1$ T) & $H \perp [1,0,0]$:
Magneto-resistance ($H = +1$ to $-1$ T) & $H \perp [1,0,0]$:
Dilatometry

MT is field independent
FCC to Monoclinic at MT

Ni$_2$MnGa

- $\Delta L/L$ [%]
- Temperature (K)

MT 197 K
PMT 214 K

H = 0T
H = 9T
**Dilatometry:** This technique measures the length change in a sample over changes in temperature and magnetic field (5-350 K, 0-9 T). This dilatometer made of OFHC copper utilizes a capacitive technique that compares a capacitor gap to the expansion or contraction of a sample. Further design details of this dilatometer can be found in G. Schmiedeshoff, et al., Rev. of Sci. Inst. 77, 123907 (2006) see below. This technique enables measurement of linear and volumetric coefficients of expansion, Grünenisen parameters and indications of sudden changes in crystal symmetry.
FIG. 1. A schematic of the capacitive dilatometer. The left panel shows a front “cut-away” view identifying parts: (a) upper (fixed) capacitor plate, (b) lower (movable) capacitor plate, (c) BeCu spring, (d) sample, (e) sample platform, (f) lock ring, (g) copper shims, (h) electrical isolation (Stycast 2850 FT and Kapton), (i) electrical isolation (Kapton washers), (j) upper guard ring, (k) lower guard ring, (l) nut, (m) 0-80 copper screws (six in total), (n) mounting plate, (o) main flange, and (p) lower flange. The right panel represents a side view of the dilatometer.
Specific Heat:

How much heat energy can you stuff in or take out of a little sample in a certain amount of time?
Specific Heat:
Specific Heat:
Specific Heat:

Vacuum
Specific Heat:

\[
T \text{ [K]} \quad t \text{ [sec]}
\]

\[
T \text{ [K]} \quad t \text{ [sec]}
\]
Specific Heat:

\[ T_1 = A_1 \exp\left\{+\frac{B_1}{\tau_1}\right\} \]

\[ T_2 = A_2 \exp\left\{-\frac{B_2}{\tau_2}\right\} \]
Specific Heat \( T = 2 - 300 \text{ K}, B = 0 \text{ g}\)
Specific Heat $T = 2 - 300$ K, $B = 10000$ g

Ni$_2$MnGa

10,000 G

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

$T$ (K)

$C_D$ [$\Theta_D = 325$ K ($\rho_D = 10.3$)]

$C_{E1}$ [$T_{E1} = 1050$ K ($\rho_{E1} = 1.7$)]

$C_e$ [$\gamma = 10.1$ mJ K$^2$ mol$^{-1}$]

$C_{calc}$
Specific Heat $T = 2 - 300 \text{ K}$, $B = 0$ to $90000 \text{ g}$

$\text{Ni}_2\text{MnGa}$

$T_M = 202 \text{ K}$
Specific Heat \((H = 0 \text{ g})\)

C/T = \(\gamma + B_3 T^2\)

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

Ni\(_2\)MnGa

\(B = 0\)

\(C/T = \gamma + B_3 T^2\)

\(\gamma = 10.0\)

\(B_3 = 0.2123\)

\(\Theta_D = 332 \text{ K}\)

\(H = 0, 100, 250, 500, 1,000, 5,000, 7,500, 10,000, 90,000 (\text{g})\)
Specific Heat \( (H = 90,000 \text{ g}) \)

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

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

\[ H = 0, 100, 250, 500, 1,000, 5,000, 7,500, 10,000, 90,000 \text{ (g)} \]
Specific Heat: Global Data \((H = 0\) to \(90,000\) g\)

\[
\text{Ni}_2\text{MnGa}
\]

\text{[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:

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

<table>
<thead>
<tr>
<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>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>10.3</td>
<td>0.2123</td>
<td>332</td>
</tr>
<tr>
<td>100</td>
<td>10.3</td>
<td>0.2121</td>
<td>332</td>
</tr>
<tr>
<td>250</td>
<td>10.0</td>
<td>0.2155</td>
<td>331</td>
</tr>
<tr>
<td>500</td>
<td>10.0</td>
<td>0.2170</td>
<td>330</td>
</tr>
<tr>
<td>1000</td>
<td>10.1</td>
<td>0.2193</td>
<td>329</td>
</tr>
<tr>
<td>5000</td>
<td>10.1</td>
<td>0.2220</td>
<td>327</td>
</tr>
<tr>
<td>7500</td>
<td>10.5</td>
<td>0.2228</td>
<td>327</td>
</tr>
<tr>
<td>10,000</td>
<td>10.0</td>
<td>0.2131</td>
<td>330</td>
</tr>
<tr>
<td>90,000</td>
<td>9.7</td>
<td>0.2131</td>
<td>330</td>
</tr>
<tr>
<td>global</td>
<td>10.1</td>
<td>0.2172</td>
<td>330</td>
</tr>
</tbody>
</table>

Normative for Magnetic Materials
Comparable to Cu

$T_{\text{range}} = 2 - 30$ K
\[
\Delta S_M = \text{Entropy Change due to M Transitions}
\]
\[
\Delta H_M = \text{Enthalpy Change}
\]
\[
\Delta S_L = \text{Entropy Change (Latent) due to PM Transition}
\]
\[
\Delta H_L = \text{Enthalpy Change (Latent)}
\]

<table>
<thead>
<tr>
<th>B (T)</th>
<th>T_M (K)</th>
<th>( \Delta S_M ) (J K(^{-1}) mol(^{-1}))</th>
<th>( \Delta H_M ) (J mol(^{-1}))</th>
<th>( \Delta S_L ) (J K(^{-1}) mol(^{-1}))</th>
<th>( \Delta H_L ) (J mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>200</td>
<td>5.6</td>
<td>1030</td>
<td>0.9</td>
<td>170</td>
</tr>
<tr>
<td>100</td>
<td>202</td>
<td>5.4</td>
<td>1000</td>
<td>0.9</td>
<td>180</td>
</tr>
<tr>
<td>250</td>
<td>202</td>
<td>5.7</td>
<td>1040</td>
<td>0.9</td>
<td>180</td>
</tr>
<tr>
<td>500</td>
<td>201</td>
<td>4.6</td>
<td>840</td>
<td>0.7</td>
<td>140</td>
</tr>
<tr>
<td>1000</td>
<td>202</td>
<td>5.5</td>
<td>1020</td>
<td>1.1</td>
<td>210</td>
</tr>
<tr>
<td>5000</td>
<td>202</td>
<td>5.4</td>
<td>1000</td>
<td>1.1</td>
<td>220</td>
</tr>
<tr>
<td>7500</td>
<td>202</td>
<td>5.0</td>
<td>930</td>
<td>1.0</td>
<td>205</td>
</tr>
<tr>
<td>10,000</td>
<td>202</td>
<td>5.2</td>
<td>970</td>
<td>1.1</td>
<td>200</td>
</tr>
<tr>
<td>averages</td>
<td>&lt;202&gt;</td>
<td>&lt;5.3&gt;</td>
<td>&lt;980&gt;</td>
<td>&lt;1.0&gt;</td>
<td>&lt;190&gt;</td>
</tr>
</tbody>
</table>

The average values given in red are probably reasonable estimates for the field-independent parameters.
Photoemission, Electrons and Gaps
Fundamentals of Photoemission:

The big three names:

Photoelectric effect

H. Hertz
Observed P.E.E. first in 1887

A. Einstein
Nobel ‘21

K. Siegbahn
Nobel ‘81

$E = hv$

$B.E. = hv - \Phi_s - K.E.$
ARPES: Angle Resolved Photoemission Spectroscopy

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

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

**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 Levels or Bands

1s\(^2\), 2s\(^2\), 2p\(^6\), 3s\(^2\), 3p\(^6\), 4s\(^2\), 4p\(^6\), ..., 6d, 7f

Fermi Energy

Outer shell Valence band

Inner shell or energy band
Energy Levels or Bands

1s\(^2\), 2s\(^2\), 2p\(^6\), 3s\(^2\), 3p\(^6\), 4s\(^2\), 4p\(^6\)....6d, 7f

As distance changes from the nucleus, electron energy and density change until the Fermi energy is reached.

What happens at the Fermi energy determines the type of energy gap.
Energy Levels or Bands

1s², 2s², 2p⁶, 3s², 3p⁶, 4s², 4p⁶, ..., 6d, 7f

Just before the Fermi Energy we can have three kinds of gaps, Band Gaps:
1) No Gap
2) Full Gap
3) Pseudo-Gap

Think of a Gap as the ability for outer electrons to reach the Fermi Energy.

What happens at the Fermi energy determines the type of gap.
Densities of States and Gaps

No Gap

Gap between last energy state and the $F_E$

Fermi Energy
A Gap becomes…

![Graph showing Fermi Energy and Density of states vs. Energy (eV). The Fermi Energy is indicated on the graph.](image)
A Gap becomes a Pseudo-Gap:

Pseudo-Gap – Distinct changes around the Fermi Energy. No excluded density of states, but fluctuations in the density of states due to temperature or field.
Band Gaps:

1) No Gap - No excluded density of states, a good metal.
2) Full Gap - Some excluded density of states, a very, very bad metal, in reality an insulator.
3) Pseudo-Gap – No excluded density of states, but fluctuations in the density of states due to temperature or field.
Temperature Dependent UV-Spectroscopy \((h\nu=21.21\text{eV})\)

![Graph showing normalized intensity vs binding energy for Ni$_2$MnGa at different temperatures.](image)
Temperature Dependent UV-Spectroscopy ($h\nu=21.21\text{eV}$)
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 Ni$_3$MnGa 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.
The story of data on a martensite metal
going bad
does not end there…
Life as a theoretical physicist.
FIG. 3 (color). The majority- and minority-spin DOS for the spin-polarized martensitic phase \( (T < T_M) \) and the spin-polarized fcc \( (T_{PM} < T < T_C) \) of \( \text{Ni}_2\text{MnGa} \). The top panel depicts the total DOS, whereas the middle and bottom panels depict the contributions due to the \( d \) electrons of the Ni and Mn atoms, respectively. The contributions due to the Ga electronic degrees of freedom are smaller by an order of magnitude and have been disregarded for the purpose of this comparison.
3-D Fermi Surface Map:

**FIG. 4** (color). Fermi surfaces in the Brillouin zones corresponding to (a) the nonmagnetic fcc phase ($T > T_C$), (b) the spin-polarized fcc phase ($T_{PM} < T < T_C$), and (c) the martensitic ($T < T_{PM}$) of Ni$_2$MnGa. Both the merged and the individual band contributions to the Fermi surface are depicted. Plots performed with XCRYSDEN [28] using the structural data from Ref. [29].

**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.

Combined Experimental and Theoretical Investigation of the Premartensitic Transition in Ni$_2$MnGa


$^1$Physics Department, Boston College, 140 Commonwealth Avenue, Chestnut Hill, Massachusetts 02467, USA
$^2$Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA
$^3$Departament d’Estructura i Constituents de la Matèria, Facultat de Física, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Catalonia, Spain
$^4$Physics Department, Temple University, Philadelphia, Pennsylvania 19122, USA
$^5$Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, United Kingdom

(Received 28 January 2008; published 23 April 2008)

Ultraviolet-photoemission (UPS) measurements and supporting specific-heat, thermal-expansion, resistivity, and magnetic-moment measurements are reported for the magnetic shape-memory alloy Ni$_2$MnGa over the temperature range 100 < T < 250 K. All measurements detect clear signatures of the premartensitic transition ($T_{PM} \sim 247$ K) and the martensitic transition ($T_M \sim 196$ K). Temperature-dependent UPS shows a dramatic depletion of states (pseudogap) at $T_{PM}$ located 0.3 eV below the Fermi energy. First-principles electronic structure calculations show that the peak observed at 0.3 eV in the UPS spectra for $T > T_{PM}$ is due to the Ni $d$ minority-spin electrons. Below $T_M$ this peak disappears, resulting in an enhanced density of states at energies around 0.8 eV. This enhancement reflects Ni $d$ and Mn $d$ electronic contributions to the majority-spin density of states.

DOI: 10.1103/PhysRevLett.100.165703 PACS numbers: 81.30.Kf, 71.20.Be, 79.60.−i
Surely you were aware when you accepted the position, Professor, that it was publish or perish.
Surely you were aware when you accepted the position, Father, that it was publish or parish.
Special thanks to some of my collaborators:

James L. Smith

Jason “Captain” Lashley
Your name here!
Thank you for listening, none of these guys ever listen to me!