

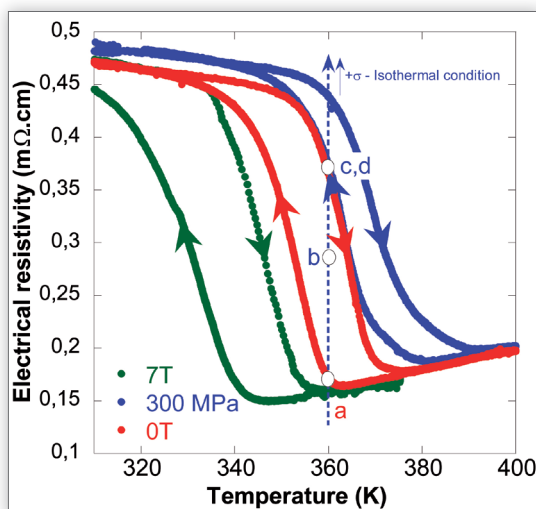
Resistivity, magnetism and shape memory in martensitic alloys

The martensitic phase transformation plays an important role in transformations of the microstructure and plasticity of many materials. The term martensite referred originally to a structural phase of carbon steel alloys named after German metallurgist A. Martens. This term has gradually been extended to other metallic alloys possessing a first order, solid to solid, phase transition of "displacive" nature (that is one where all the atoms shift slightly, all together at the same time, without any long-range diffusion of the alloy's different atoms). The resulting lattice deformation leads to a new crystal structure with new properties. Certain ferromagnetic alloys of nickel, manganese and a third element such as gallium constitute a particularly interesting case. Under application of magnetic field or pressure, they exhibit large changes of electrical resistivity, entropy or magnetization, and even an astonishing ability to change shape reversibly. These are properties which have promising industrial applications in actuators, current limiters, switches, refrigerators.

The alloys of interest here are the so-called "Heusler" alloys of formula Ni_2MnX (where element $X = Ga, In, Sn, Sb, \dots$). The parent phase of the martensitic transition is "austenite" (another name from steel-making history). Because of the symmetry-lowering during the structural phase transition, the nucleation of the martensite phases within a crystal of the austenite phase, induced by cooling, allows multiple structural configurations with different orientations that are called "variants".

Due to its displacive nature, the transformation proceeds by cooperative movements of the atoms, keeping the same atomic order as the austenite parent phase. The nucleation of a single martensite variant within an austenite crystal would require an enormous elastic energy. This energy is greatly reduced when there is an additional lattice invariant shear to the homogeneous lattice deformation occurring by "slip" or "twinning". A modulated martensite structure usually appears and consists of building blocks of the structure twinned in a way to compensate for the difference in the martensite and austenite lattice constants. A thermal hysteresis consequently appears, because there is a frictional barrier opposing the interfacial motion of the nucleating phase.

A subtle balance between the structural and magnetic states resulting from the off-stoichiometry (deviations with respect to the precise base-formula Ni_2MnX) allows a wide range of multi-functional properties. When pressure or a magnetic field is applied, a large strain or a change in shape (of up to 10% in Ni-Mn-Ga alloys) can be induced via a structural reorientation of the martensite variants by twin-boundary motions. The variant selection depends on its shear strain or its magnetic moment with respect to the applied stress or magnetic field. The original shape can be recovered by heating above the structural transition temperature (the "shape-memory" effect).



Another very interesting property is the shift of the martensitic transformation temperature on application of pressure or a magnetic field, see Fig. 1, which shows resistivity data for the case of a Ni-Mn-In alloy with some Cobalt. The transition is shifted towards higher temperature under pressure and towards lower temperature under magnetic field. Thus, at fixed temperature, large magnetoresistance effects, or piezoresistance effects (e.g. the vertical line in Fig. 1) of up to several hundred %, are observed.



Fig. 2: Optical microscope images of a single crystal of NiMnIn alloy under increase and release of pressure, showing irreversibility of the transformation of the crystal's microstructure if pressure is applied and released at a cooling point in the hysteresis cycle. Arrows σ show the applied uniaxial stress direction (squeezing direction).

These effects are the direct consequence of the possibility to transform the austenite phase into a martensite phase by applying a pressure, and to transform martensite into austenite by applying a magnetic field.

The process can be fully reversible, or irreversible (see Fig. 2), depending on whether the external field is applied during the heating or the cooling branch of the hysteresis. There is thus a large range of possibilities for coupling the different functional properties of these materials for application to new sensors, switches, actuators, and other devices.

Fig. 1: Three hysteresis loops for the resistivity of a $Ni_{45}Co_5Mn_{37.5}In_{12.5}$ single crystal as it is temperature-cycled through the transition from austenite (at high T) to martensite (at low T). The red loop is for zero field, zero pressure. Applying a magnetic field (green loop) shifts the transition temperature down, applying pressure (blue loop) shifts it up. At fixed temperature (360 K), the material can be transformed through different states a, b... by varying the pressure.

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FURTHER READING

"Large piezoresistance and magnetoresistance effects on $Ni_{45}Co_5Mn_{37.5}In_{12.5}$ single crystal"

L. Porcar, D. Bourgault and P. Courtois

Appl. Phys. Lett. 100, 152405 (2012).

"Irreversibility of the martensitic transformation in Ni-Mn-In single crystal studied by resistivity under pressure and in situ optical observations"

L. Porcar, P. Courtois, G. Crouigneau, J. Debray and D. Bourgault

Appl. Phys. Lett. 105, 151907 (2014).