# Magneto-caloric Effect and Magnetic Field Induced Strain of Heusler Alloys

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## Abstract

Heusler Alloys are alloy compounds with the molecular formula $X_2YZ$, where X and Y are transition-series elements and Z is from the s or p group. They are found to be of immense significance due to certain characteristics such as shape memory, half-metal nature and the Magneto-Calorific Effect (MCE). In this short summer-project that I was involved in at the Indian Institute of Technology, I studied the MCE effect in Heusler Alloys using a Vibrating Sample Magnetometer (VSM) and the Calorimeter.

## 1. Shape Memory

Shape Memory, as the name suggests, is the tendency of a body to assume a certain form upon variations of external conditions such as temperature. It usually refers to the tendency of a body to "remember" its original form before deformation and transition by heating. There are two forms of structure in such compounds: the Martensite and Austernite forms. The physical understanding of shifts between the two forms can be thought of in terms of the molecular lattice structure in case of Shape Memory Alloys (SMA). Such compounds usually assume the L21 lattice structure that has 4 interpenetrating FCC unit cells.

Martensite is a crystal structure that is formed by displacement transformation, as opposed to the common diffusive transformations, which is much slower. For reversible martensitic transformation to occur, the following conditions must be satisfied:

1. the driving force for the transformation should be small
2. the interface between the martensite and the austenite phases has to be mobile upon heating and cooling
3. the transformation should be crystallographically reversible.

Martensitic transformations are usually first order solid state structural phase transitions. The atoms move in an organized manner relative to their neighbors and therefore they are known as 'military' transformations in contrast to diffusion-based 'civilian' transformations. And the displacement can be described as a homogeneous lattice deformation.

The temperature ranges over which the Martensite and the Austernite states exist are defined by Ms and Mf temperatures (Start temperature and Finish temperature for Martensite phase) and similarly, the Ts and Tf temperatures for the Austernite phase. The cycle over which SMAs change from the Martensite phase to the Austernite phase by the application of heat and then from the Austernite phase to the Martensite phase by rapid cooling is characterized by a hysteresis curve with a loss of energy as heat.

Upon application of heat, lattice structures change. For instance, if the Martensite structure has a cubic structure, upon heating, the lattice points may extend in a single direction to give a tetragonal shape in the Austernite phase. Such shape 'memories' may be unidirectional (where the body tends to retake its shape in either of the phases and never in the other) or bidirectional.

## 2. Magnetic Entropy ($S_m$)

Entropy refers to the disorderliness of a system, in terms of state variables of its constituent entities. As shown in the illustration. A ferromagnetic material (Fig 2.a) has strong magnetization in the direction of the external magnetic field. An anti-ferromagnetic material has equal magnetization in the direction and opposite to the direction of the magnetic field.

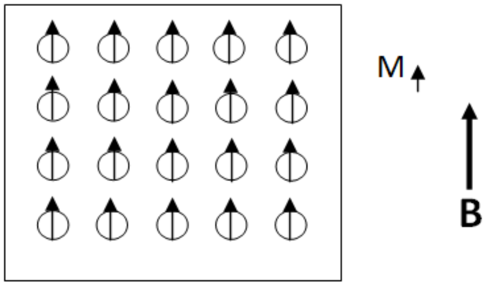


Fig 2.a

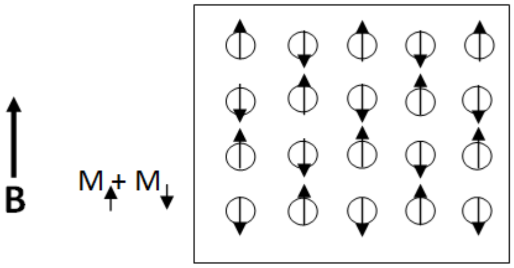


Fig 2.b

For anti-ferromagnetic material, $M_{\downarrow}$ and $M_{\uparrow}$ exactly nullify each other. However, in ferromagnetic materials, there is some net magnetization in one of the directions. In Heusler alloys, the constituents of the alloy define the magnetic character of the alloy. The table below shows some examples of Heusler Alloys and their magnetic properties.

| Heusler Alloy | Magnetic Character |
|---|---|
| $Mn_2VAl$ | Ferrimagnetic |
| $Fe_2VAl$ | Non-Magnetic |
| $Co_2MnSi$ | Ferromagngtic |

By changing from one state with a certain magnetic property to another state with a different distinct property, we are bringing in magnetic entropy changes. By partial doping of certain elements in a Heusler Alloy, the magnetic character can be manipulated.

Now, given that there is entropy associated with such systems, one can associate heat evolved as entropy changes take place. This heat evolved is the result of what is termed as Magneto-Calorific Effect.

## 3. Ferromagnetic Shape-Memory Alloys (FSMAs)

The idea of temperature-dependent shape-memory can be extended to magnetic-field dependent FSMA shape-memory. One can think of the physical picture in terms of alignment of domains upon the application of external magnetic field. This property of the FSMAs is often used to generate Magnetic Field Induced Strain (MFIS), which can be applied in various ways such as in electric circuit switches.

## 4. Half-Metallic Nature of Heusler Alloys

Heusler Alloys display half-metallic character.

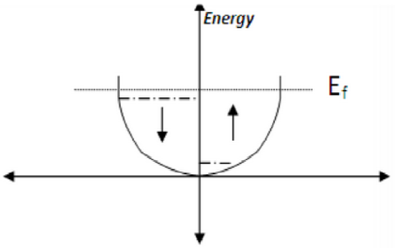


Fig 3.a

In general, the number of spin-electrons and spin-down electrons are same and upon application of same and upon application of external magnetic field, some of the external magnetic field, some of the electrons in one of the states electrons in one of the states (depending upon the direction of field) are shifted from one spin state to the other, as shown in Fig 3.a. In these materials the two spin bands these materials the two spin bands show a completely different behavior. While the majority spin band (referred also as spin-up band) shows the typical metallic behavior, the minority spin band (spin band) exhibits a semiconducting behavior with a gap at the Fermi level. Therefore such half ferromagnets and can be considered as hybrids between metals and semiconductors. This has been ferromagnets and can be considered as hybrids between metals and semiconductors. This has been ferromagnets and can be considered as hybrids between metals and semiconductors. This has been illustrated in Fig 3.b.

But for half-magnetic behavior, we have the energy profile for spin-states as shown in Fib 3.b. As can be seen there is a distinct band-gap between the localized energy profiles for the spin-up state in the graph. This marks the fully-polarized state that I exploited as the half-magnetic property.

Adding the spin degree of freedom to the conventional electronic devices has several advantages like non-volatility, increased data processing speed and decreased power consumption. The current advances in new materials speed and especially in the metals are promising for engineering new spintronic devices in the near future.

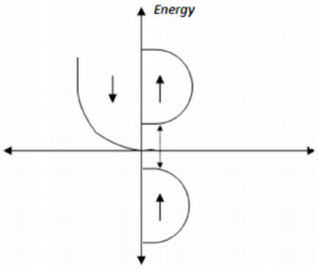


Fig 3.b

## 5. Magnetic Field Induced Strain (MFIS)

The MFIS phenomenon is seen in Heusler Alloys. The physical understanding of this effect can be found in the structural changes effected by magnetization in a lattice. It can be thought of as the structural changes effected by magnetization in a lattice. It can be thought of as a giant the structural changes effected by magnetization in a lattice. It can be thought of as a magnetostrictive effect. Dimensional changes of 10% have been realized with Magnetic Field Induced Strain.

## 6. Magneto-Calorific Effect

The mathematical treatment of the MCE effect has been studied:

The internal energy of a system can be represented either as $U = U(S, V, H)$ or $U = U(S, V, M)$ where $M$ is the Magnetic Moment, $H$ is the Magnetic Field, $S$ is the Entropy and $V$ represents the Volume. Correspondingly the differential $dU$ can have the forms:

$$dU = TdS - pdV - MdH \text{ or } dU = TdS - pdV - HdM$$

…(1)

The *Free Energy (F)*, which is a function of Temperature, Volume and Magnetic Field (H), is used for systems with constant volume and is defined as $F = U - TS$. Its differential is given by

$$dF = -SdT - pdV - MdH$$

…(2)

The *Gibbs Free Energy (G)* is a function of Temperature, Pressure and Magnetic Field (H) and is used for systems under constant pressure. It is defined as $G = U - TS + pV - MH$. Its differential is given by

$$dG = -SdT + Vdp - MdH$$

…(3)

For the free energy F the internal parameters Entropy, Pressure and Magnetic Moment (M), conjugated to the external variables Temperature, Volume and Magnetic Field (H), can be determined by the following equations of state

$$S(T, H, V) = -\left(\frac{\partial F}{\partial T}\right)_{H, V}$$

…(4)

$$M(T, H, V) = -\left(\frac{\partial F}{\partial H}\right)_{T, V}$$

…(5)

$$p(T, H, V) = -\left(\frac{\partial F}{\partial V}\right)_{H, T}$$

…(6)

Analogously, we have

$$S(T, H, p) = -\left(\frac{\partial G}{\partial T}\right)_{H, p}$$

…(7)

$$M(T, H, p) = -\left(\frac{\partial G}{\partial H}\right)_{T, p} \ldots\ldots\ldots (2)$$

…(8)

$$V(T, H, p) = \left(\frac{\partial G}{\partial p}\right)_{H, T}$$

…(9)

Using (4) – (9),

$$\left(\frac{\partial F}{\partial T}\right)_{H,V} = \left(\frac{\partial G}{\partial T}\right)_{H,p}$$

…(10)

$$\left(\frac{\partial F}{\partial H}\right)_{T,V} = \left(\frac{\partial G}{\partial H}\right)_{T,p}$$

…(11)

$$\left(\frac{\partial F}{\partial V}\right)_{H,T} = -\left(\frac{\partial G}{\partial p}\right)_{H,T}$$

…(12)

The Heat Capacity $C_x$ at constant variable $x$ is defined by

$$C_x = \left(\frac{\partial Q}{\partial T}\right)_x$$

…(13)

where $\delta Q$ is the heat quantity changing the system temperature on $dT$. By II$^{nd}$ Law of Thermodynamics,

$$\delta S = \frac{\partial Q}{T}$$

…(14)

$$C_x = T\left(\frac{\partial S}{\partial T}\right)_x$$

…(15)

The bulk thermal expansion coefficient can be represented by $\alpha_T = \alpha_T$ (T, H, p). Since

$$\alpha_T V = \left(\frac{\partial V}{\partial T}\right)_{H,p}$$

and equation (11) applies,

$$\alpha_T = -\frac{1}{V}\left(\frac{\partial S}{\partial p}\right)_{H,T}$$

…(16)

Now, $dS = \left(\frac{\partial S}{\partial T}\right)_{H,p} dT + \left(\frac{\partial S}{\partial H}\right)_{T,p} dH + \left(\frac{\partial S}{\partial p}\right)_{H,T} dp$

…(17)

Using equations (10), (15), (16) and (17), and setting $dS = 0$ for an adiabatic process,

$$\frac{C_{H,p}}{T} dT + \left(\frac{\partial M}{\partial T}\right)_{T,p} dH - \alpha_T V dp = 0$$

…(18)

where $C_{H,p}$ is the heat capacity under constant magnetic field and pressure.

Under an *adiabatic–isobaric process* (*dp = 0*, this process is usually realized in Magnetocaloric experiments) the temperature change due to the change of the magnetic field (the Magnetocaloric effect) can be obtained as

$$dT = -\frac{T}{C_{H,p}}\left(\frac{\partial M}{\partial T}\right)_{H,p} dH$$

…(19)

Now, defining the Bulk Modulus κ as

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T,H}$$

For an *adiabatic–isochoric process* (dV = 0) the total differential dV has the form

$$dV = \alpha_T V dT + \left(\frac{\partial V}{\partial H}\right)_{T,p} dH - \frac{V}{\kappa}\, dp = 0$$

…(20)

Using (18) and (20),

$$\left[\frac{C_{H,p}}{T} - \alpha_T^2 \kappa V\right] dT + \left[\left(\frac{\partial M}{\partial T}\right)_{H,p} - \alpha_T \kappa \left(\frac{\partial V}{\partial H}\right)_{T,p}\right] dH = 0$$

The second term is found to be small and thus can be neglected.

Hence, the equation of Magne
Effect is given by

$$\boldsymbol{dT = -\frac{T}{C_{H,p}}\left[\left(\frac{\partial M}{\partial T}\right)_{H,p} - \alpha_T \kappa \left(\frac{\partial V}{\partial H}\right)_{T,p}\right] dH}$$

Where, the second term is due to the internal magnetostrictive tensions arising from the change in magnetic state of the system keeping the volume constant. This way on can see that change of magnetization with temperature leads to heating or cooling.

One can analyze the various cases for the given equation.

1. If $C_{H,\ p}$ is high, the change in temperature will be low, which is true for the property of heat capacity.
2. If $\left(\frac{\partial M}{\partial T}\right)_{H,p} > \alpha_T \kappa \left(\frac{\partial V}{\partial H}\right)_{T,p}$ then heating occurs. For $\left(\frac{\partial M}{\partial T}\right)_{H,p} < \alpha_T \kappa \left(\frac{\partial V}{\partial H}\right)_{T,p}$ cooling occurs. If the magnetization produced for unit change in temperature is less than the internal magnetostrictive tensions used for keeping the volume constant, the heat generated will be used up for the latter and thus cooling occurs. A similar line of thought can be employed to argue for the case of heating.
3. The effect is stronger at higher temperatures (T) as can be observed in the equation.

# Experimentation

### *Preparation of Samples*

The process used for preparation of Heusler Alloy sample for analysis involves arc-melting, using which the alloy ingots were obtained. Elemental powders of Nickel (Ni), Gallium (Ga) and Manganese (Mn), as per the target composition, are weighed in a calibrated electronic balance and blended thoroughly. The blended alloy mixture is cold-compacted in a stainless steel die under a pressure of 40 Mega-Pascal.

The compacted pellet is placed in the water-cooled copper hearth of the arc furnace and the chamber is pumped down to around $10^{-5}$ Torr.

The chamber is purged with Argon gas to remove traces of oxidizing atmospheric gases and finally filled with argon gas pressure of 750 Torr. A DC arc is then struck and the pellet is melted. The cast ingot is then flipped around and re-melted 3-4 times to ensure complete melting of the constituent elements.

The alloys thus obtained are brittle and also need to be homogenized further to obtain samples with consistent properties. The metallic ingots cannot be heat treated in air since they might oxidize. So, the as-cast ingots are taken separately in fused silica ampoules, which are pumped down to $10^{-5}$ Torr and then flame-sealed. The vacuum-sealed ampoules containing the alloy ingots are placed inside a raising hearth furnace, homogenized at 1423 K for 24 hours and allowed to slowly cool inside the furnace. The slowly cooled samples do not show any signature of Martensitic transformations in Differential Scanning Calorimeter (DSC) studies. So, the cylindrical ingots are cut into small discs and cleaned with Acetone ($CH_3$—CO—$CH_3$) in an ultrasonic bath.

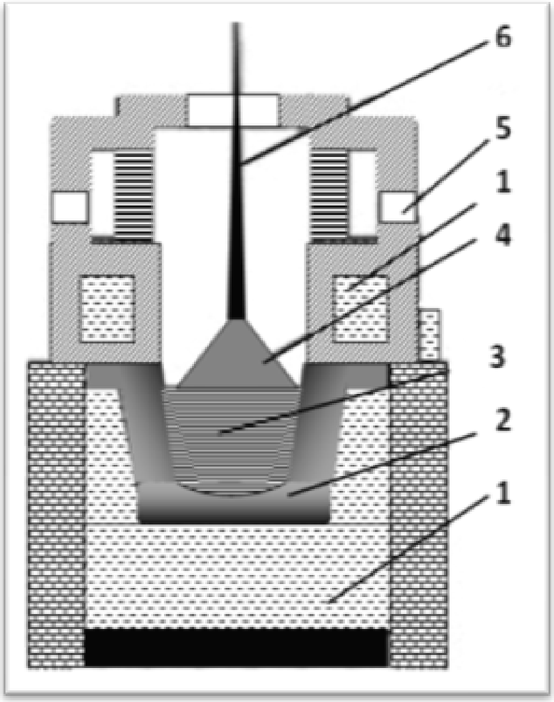


**Figure:** ***Labels***
1. Circulating water to cool the hearth,
2. Copper hearth
3. Compacted metal blend
4. Electric arc struck between the electrodes
5. Gas inlet valve
6. Water cooled flexible electrode with tungsten tip (*anode*).

**Figure 4**

The dried discs are again flame-sealed in fused silica ampoules at a pressure of $10^{-5}$ Torr, annealed separately at various temperatures for 6 hours and quenched. Air, ice water and liquid nitrogen are used as quenching media for different investigations. Thick discs (8 mm thickness) are annealed at 1273 K and quenched in ice water for mechanical testing (Stress - Strain studies).

### *Characterization*

#### Differential Scanning Calorimeter (DSC)

Differential Scanning Calorimeter is a device used for thermo-analytic studies in which the difference in the amount of heat required to increase the temperature of a sample and a reference material is measured as a function of temperature.

The DSC curves are recorded either under a constant heating (or cooling) rate or under isothermal conditions. A typical DSC consists of two isolated sealed pans, one containing the sample and the other a reference material.

The two pans are heated or cooled uniformly while the heat flow difference between the two is monitored.

The basic principle underlying this technique is the following: when the sample undergoes a physical transformation such as phase transition, more or less heat will need to flow to it in comparison with the reference in order to maintain both at the same temperature.

In the power compensation type DSC, heat is supplied to either of the pans so that both are maintained at the same temperature. The heat flow (dH/dt) is then estimated from this data.

In a DSC based on the heat-flux technique, the temperature difference (ΔT) between the two isolated pans is measured from which the heat flow is estimated.

For a Shape-Memory Alloy such as a Heusler Alloy, the DSC curve obtained is shown in Figure 5. We can see distinct representation for the temperatures Ms, Mf, As and Af.

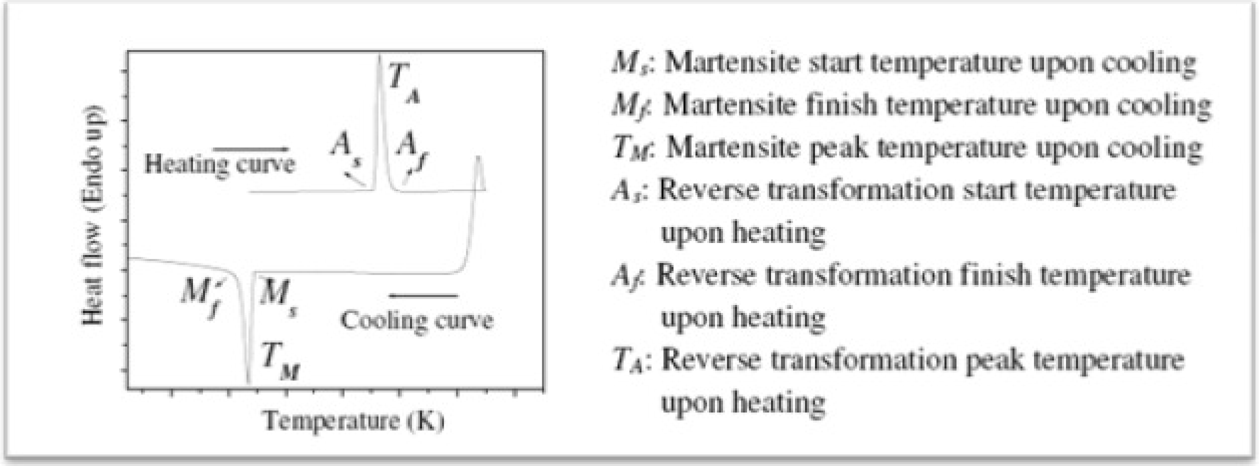
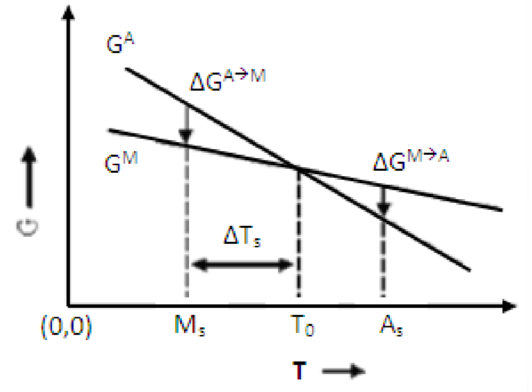


**Figure 5**



The free energy of the martensite phase is more than that of the austenite phase. Thus, during the solid state phase transformation from martensite to austenite, energy is absorbed by the system (endothermic reaction).

Similarly, during the transformation from austenite to martensite, energy is released from the system (exothermic reaction). The Gibbs free energy change of a system at M « A transformation may be written as,

$$\Delta G = \Delta G_c + \Delta G_s + \Delta G_e = \Delta G_{nc} + \Delta G_c$$

Where $\Delta G_c$ is a chemical energy term originating in the structural change from parent to martensite and $\Delta G_{nc}$ is the non-chemical energy term contains a surface energy term ( $\Delta G_s$ between austenite and martensite) and elastic energy term ( $\Delta G_e$ around the martensite).

$$\Delta G_c = \Delta H - T_0 \Delta S = 0$$

In most martensitic transformations, $\Delta G_{nc}$ is equally large as $\Delta G_c$. In the absence of elastic strain energy, the forward and reverse transformation temperatures (i.e. Ms and As) coincides with the thermodynamic equilibrium ( $\Delta G = 0$) temperature $T_0$.

This non-chemical energy term changes the driving forces and hence $T_0$. A further super-cooling of $\Delta T_s$ from $T_0$ is necessary for inducing the Martensitic transformation and superheating is necessary for the reverse Martensitic transformation.

The fact that the Martensitic Start and Finish temperatures are not the same can be explained in a similar way. Elastic energy around the martensite resists the growth of the martensite unless a further driving force such as cooling is performed on the system.

**Vibrating Sample Magnetometer (VSM)**

The VSM is used usually for studying Hysteresis Curves, where the dependence of magnetic moment of a sample to the external magnetic field is analyzed.

For studying the Magnetocaloric Effect, we study the magnetization as a function of temperature.

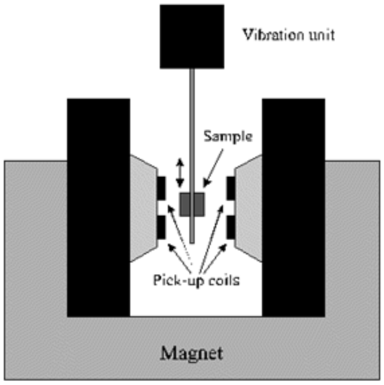


Figure 6

A sample is placed inside a uniform magnetic field to magnetize the sample. The sample is then physically vibrated, typically through the use of a piezoelectric material. The induced voltage in the pickup coil is proportional to the sample's magnetic moment. It, however, does not depend on the strength of the applied magnetic field. In a typical setup, the induced voltage is measured through the use of a lock-in amplifier using the piezoelectric signal as its reference signal.

One expects to observe a curve that comprises of two kinds of transformation: Ferromagnetism-to-Paramagnetism and Austenite-to-Martensite. The former is represented in an M vs. T graph as the dip in the curve profile at the Curie temperature. For the latter, hysteresis is observed in the curve besides the appearance of peaks in the regions between $A_s$ and $A_f$, and between $M_s$ and $M_f$. The hysteresis can be explained by considering that for phases such as the Martensitic phase, the lattice-units are held in position by the surrounding lattice structure in such a manner that a greater energy is needed to bring about an appreciable change in the magnetization than for the Austenitic phase. In other words, the heat lost, represented in the curve area, is used up for the transformation.

However, in some cases, as in our sample, the transformation temperature and the Curie temperature are very near each other. In such a case, the peaks observed at transformation temperatures disappear. We only obtain a smooth decline in the curve although hysteresis is present, implying a first order transition in the state.

## Strain Gauge

The strain gauge has been used for studying the Magnetic-Field Induced Strain (MFIS) in $Ni_{50}Mn_{30}Ga_{20}$ alloy. A Strain Gauge essentially works on the principle of variation of resistance due to change in the strain in the Gauge. Usually, it constitutes an arm of a Wheatstone Bridge that, because of the change in strain, leads to a visible change in the balancing condition.

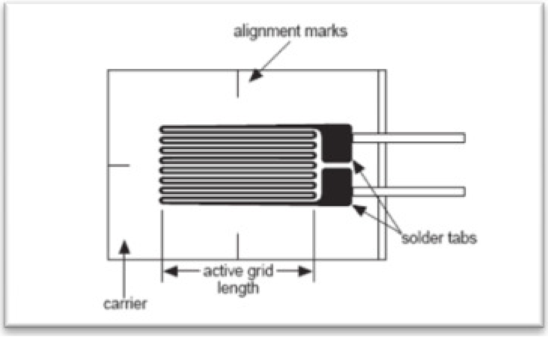


Figure 7

The metallic strain gauge consists of a very fine wire or, more commonly, metallic foil arranged in a grid pattern. The grid pattern maximizes the amount of metallic wire or foil subject to strain in the parallel direction. The grid is bonded to a thin backing, called the carrier, which is attached directly to the test specimen.

A fundamental parameter of the strain gauge is its sensitivity to strain, expressed quantitatively as the gauge factor (GF). Gauge factor is defined as the ratio of fractional change in electrical resistance to the strain developed.

$$Gauge\ Factor = \frac{\Delta R/R}{\Delta l/l}.$$

For my study, the Gauge factor on the catmanEASY interface was set to 2.

The general Wheatstone bridge, illustrated below, consists of four resistive arms with an excitation voltage, $V_{exc}$ that is applied across the bridge.

$$V_0 = [\frac{R_3}{R_3 + R_4} - \frac{R_2}{R_2 + R_1}]V_{exc} \quad \ldots\ldots\ldots\ldots\ldots(S)$$

If we replace any of the arms of a balanced Wheatstone bridge with a Strain Gauge and introduce strain in it, we get an unbalanced bridge. If the nominal resistance of the Gauge is $R_G$ then the change in resistance due to strain can be expressed as

$$\Delta R = R_G * Gauge\ Factor * Strain$$

Now putting $R_1 = R_2$, $R_3 = R_G$ and $R_4 = R_G + \Delta R$ (initially, before strain is applied, $R_4 = R_G$) in (S)

$$\frac{V_0}{V_{exc}} - \frac{Gauge\ Factor * Strain}{}\left(\frac{1}{1+Gauge\ Factor * \frac{Strain}{2}}\right)$$

In this experiment, we firstly have to do the calibration for the Strain Gauge. For this, I took a reference sample that had predetermined values for Strain for given values of external magnetic field.

After this, the data for the sample is taken and the calibration is used to get the final calibrated value. The interface used, for my study, was catmanEASY with a Strain Gauge 120 Ω Transducer with a Bessel Filter of 5 Hz and Gauge Factor of 2. The Excitation Voltage was kept at 5 V.

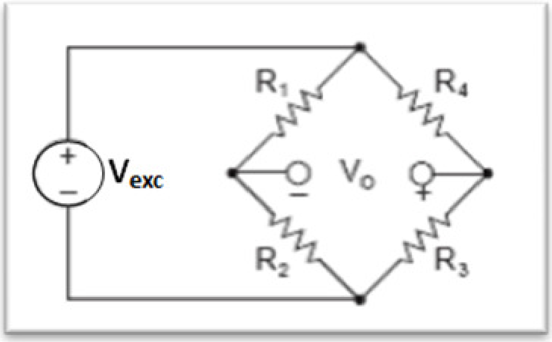


Figure 8

The expected result is the development of, and increase in, strain with increasing magnetic field. The highest strain developed in the alloy-system being studied that has been reported is 10%. However, the strain developed can be due to compression or elongation as per the material's behavior towards a given external magnetic field.

# Conclusion

Shape Memory, Magnetic Field-Induced Strain (MFIS) and Half Metallic Nature of Heusler Alloys were studied. The Magnetocaloric effect is analyzed and the governing equation is derived.

Experimental methods are explored. The techniques for preparation and characterization of Heusler Alloys are studied.

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