Title: Production and Characterization of Fe-based metallic glasses

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Resum

Las aleaciones amorfas metálicas fueron descubiertas en el 1960. Desde aquel momento, los científicos no han dejado de investigarlas para mejorar sus propiedades y encontrar nuevas aplicaciones. La innovación en esta técnica ha permitido la creación de materiales funcionales y estructurales con propiedades desconocidas hasta ahora y que tienen algunas características que pueden ser de gran utilidad para aplicaciones de ingeniería.

El objetivo de este proyecto es la producción de tres aleaciones de aceros amorfos, Fe$_{71.2-x}$C$_{7.0}$Si$_{3.3}$B$_{5.5}$P$_{8.7}$Cr$_{2.3}$Al$_{2.0}$Mo$_{x}$ (x=0, 4.5 and 6.5 at%), por el método de solidificación rápida con rueda de cobre (melt-spinning technique). Este trabajo presenta una detallada descripción del equipo usado para producir estas cintas.

Los vidrios metalicos basados en Fe han sido caracterizados con microscopía electrónica y difracción de rayos X que permiten conocer la composición real de las muestras y si la estructura atómica es o no es amorfá. La espectroscopía Mössbauer de transmisión (TMS) permite estudiar el entorno local de los átomos de Fe en el estado vitriy y muestra los cambios en la estructura amorfa debido a la adición de Mo. Se observa una reducción del campo medio hiperfino a medida que la cantidad de Mo crece.

Además, se han estudiado las tres muestras con calorimetría (DSC) para encontrar la temperatura de transición vitriy y decidir las temperaturas más adecuadas para los tratamientos térmicos para relajar los vidrios. Por último, se han analizado las cintas relajadas con TMS para estudiar la estabilidad de las aleaciones y el efecto de los cambios locales de estructura.

Las conclusiones obtenidas a lo largo del proyecto se pueden resumir del siguiente modo. En la aleación con un contenido intermedio de Mo, la reducción del campo hiperfino se asocia a la sustitución del Fe por el Mo en una estructura magnética desordenada rica en Fe, mientras que para la aleación con alto contenido relativo de Mo, ésta estructura es destruida llevando a un aumento del entorno paramagnético. La relación entre la GFA de estas aleaciones y sus estructuras locales determinadas por TMS es también discutida.
Overview

Amorphous metallic alloys were developed at 1960. Since then, scientists have not stopped researching in order to improve their properties and find new applications. The innovation in techniques has let to the creation of functional structural materials with unknown properties until now, that have certain properties that could be of great utility for engineering applications.

The aim of this project is to produce three amorphous steel alloys, Fe$_{71.2-x}$Cr$_{2.3}$Al$_{2.0}$Mo$_x$ (x=0, 4.5 and 6.5 at%) by the melt-spinning technique. This work presents a detailed description of the basic equipment to produce these ribbons.

The Fe-based metallic glasses were then characterized by electronic microscopy and X-ray diffraction that allow us to know the real composition of the ribbons and if the atomic structure is or is not amorphous. Transmission Mössbauer spectroscopy (TMS) allows us to study the local environments of the Fe atoms in the glassy state, showing the changes in the amorphous structure due to the addition of Mo. A reduction of the mean hyperfine field is observed as the amount of Mo increases. Moreover the three alloys were studied with differential scanning calorimetry (DSC) to find the glass transition temperature and to decide the suitable temperature of the heat treatments to relax the glasses. Finally, the relaxed samples were analyzed again with TMS in order to see the stability of the alloys and the effect of the local structure changes.

The main conclusions reached during the project can be summarized as follows. In the alloys with intermediate Mo content, the hyperfine field reduction is associated to the substitution of Fe by Mo in a disordered magnetic Fe-rich structure, whereas for the alloys with high Mo content, this structure is destroyed leading to an increase of paramagnetic environments. The relationship between the GFA of these alloys and their local structure determined by TMS is discussed.
CHAPTER 1. INTRODUCTION

Amorphous metallic alloys, also called metallic glasses (MGs), were first developed forty years ago. Such alloys present certain characteristics and properties that are unusual for solid materials and represent a new opportunity for the development of new alloys for engineering applications. These materials have been the subject of large studies during the last years, focusing on their magnetic and mechanical properties, new techniques of glass production and the design of new compositions. In addition to their fundamental interest, metallic glasses also became commercially important when Fe-based compositions were found to have good soft-magnetic properties. In this context, the present thesis reports the study of the production of an Fe-based metallic glass with the melt-spinning technique, its characterization and its thermal stability. The composition chosen for this work was \( \text{Fe}_{71.2-x} \text{C}_{7.0} \text{Si}_{3.3} \text{P}_{8.7} \text{Cr}_{2.3} \text{Al}_{2.0} \text{Mo}_x \) with \( x = 0, 4.5, 6.5 \) at.\% [1] using hot metal and pure commercial materials. This alloy was chosen because it can be produced as a bulk (amorphous rods with a maximum diameter of 6 mm) and because of its relatively high content in Fe with respect the Fe-based bulk metallic glasses (BMGs). Moreover, small amounts of Mo have been systematically substituted for Fe to check its effect on the glass forming ability (GFA) of the alloy, that is, the ease of devitrification. The obtained alloys were analyzed by x-ray diffraction to assure its amorphous character and by electron microscopy to determine the real composition. The effect of Mo substitution on the amorphous structure is discussed in terms of Transmission Mössbauer Spectroscopy (TMS) because this spectroscopic technique allows to study the local atomic order surrounding a particular Fe atom. The samples were also annealed up to several temperatures in order to determine the glass transition temperature and to study the thermal stability of these alloys. The annealed alloys were again analyzed with TMS in order to see the effect of the temperature in the local structure. The aim of this thesis was, first of all to optimize the production method of the alloys; secondly to characterize them and finally, from the TMS results, to relate the GFA of the alloys with the local structure surrounding the Fe atoms.

The structure of the present work is as follows. At the beginning, an introduction to metallic glasses is presented, from their history to their basic properties. Following, the techniques used to produce and characterize the alloys are described. In particular, the arc melting and the melt spinner technique are explained in detail, as well as, the fundamentals of Mössbauer spectroscopy. The most usual characterization techniques used in this work (X-ray diffraction, scanning electron microscopy and differential scanning calorimetry) are explained in the appendixes. After the production methods, the obtained results are presented and discussed, and finally, the work finishes with the conclusions and an outlook of the further work that can be done.
CHAPTER 2. METALLIC GLASSES

Metallic glasses, or amorphous metals, are a new class of engineering materials. They have a disordered, non-crystalline structure in the solid phase with an atomic arrangement without a long range periodicity. In the case of Fe-based metallic glasses, a 3d-transition (TM) metal is combined with metalloid (B, C, P, Si) and metallic (Al) elements to stabilize the amorphous state. These types of alloys are usually magnetic, with low coercivity and high electrical resistance. Amorphous alloy ribbons can be prepared by a continuous rapid quenching process from a molten state with a cooling rate of $10^5 - 10^6$ degrees per second using a melt spinner.

2.1 History

Metallic glasses were discovered over forty years ago when rapid quenched methods were first applied to liquid metal alloys. The first metallic glass produced by direct quenching from the melt in the laboratory (Au$_{75}$Si$_{25}$) was made by Professor Paul Duwez and co-workers at the Massachusetts Institute of Technology in 1957. During the past several years, various advances have been made in this field as a result of the discovery and development of several families of alloys with a substantially improved glass forming ability [2]. Previous metallic glasses were generally formed by cooling the melt at rates of $10^5 - 10^6$ K s$^{-1}$, causing the retention in the solid at ordinary temperatures of the random atomic structure of the liquid. The problem resides in that with this cooling rate it is difficult to obtain alloys with geometries different of ribbons, wires or foils, thus reducing their potential applicability in the industry. Since some years ago some metallic glasses with dimensions of the order of millimeters have been obtained (Bulk Metallic Glasses, BMG) requiring cooling rates of only $10^2$ K s$^{-1}$ [3].

2.2 Basic principle

A glass is a liquid that has been cooled to a rigid condition rapidly enough to avoid crystallization. The process of nucleation and growth of crystalline phase can be kinetically bypassed in some alloy melts to yield a frozen liquid configuration. Every alloy can form a glass if it is cooled rapidly enough to prevent the atoms to reach the appropriate position. This is the case of metallic glasses (MGs).

The process of glass obtention from a melt is as following. Once obtained the molten alloy, as the temperature is reduced, at some moment the melting temperature ($T_m$) will be passed. At this point, if the atoms have enough time to reorganize themselves in an ordered way, a crystalline solid is formed: the formation of an ordered system takes a certain amount of time since the molecules must move from their current location to energetically preferred points at the nodes of the crystal lattice. Instead, if the cooling rate is fast enough, molecules never reach their equilibrium position and the substance enters into dynamic arrest and a disordered, glassy solid forms. This solid
retains the same random atomic structure of the liquid at ordinary temperatures. To attain this state a certain temperature, the glass transition temperature ($T_g$), must be passed. In the region in between $T_f$ and $T_g$ the alloy is still in the liquid state (the so called undercooled liquid) and, as the atoms are compressed, it is characterized by a continuous decrease of the specific volume that reverts in a reduction of the atom mobility. **When the atoms can't be compressed more, the time required to order themselves is bigger than cooling time, and a glass is formed at the glass transition temperature ($T_g$).** Thus, the viscosity of the undercooled liquid continually grows, allowing a certain degree of atomic movement but so slow that is negligible on the experimental time scale. The glass transition temperature is defined as the temperature at which the viscosity of the liquid is $10^{13}$ Poise.

![Specific volume-temperature diagram](image)

**Fig. 2.1 Specific volume-temperature diagram for the comparison of the glass transition and crystalline transition.**

All this process can be easily followed in a specific volume versus temperature graph, as shown in **Fig. 2.1**. Above $T_f$ the stable phase is the liquid because it has the minimum energy at this pressure and temperature; a slow cooling usually leads to the freezing of the liquid at $T_f$ into a crystalline solid, that is another stable phase. This transition is marked by an abrupt discontinuity in the specific volume and the enthalpy of the alloy (curve 1 in figure 2.1). At sufficiently high cooling rates, however, many materials display a different behaviour and follow route 2 in figure 2.1 to the solid state. $T_f$ is bypassed, and the liquid state persists in a metastable phase until the lower temperature $T_g$ is reached and the second solidification scenario occurs. In a narrow temperature range near $T_g$, the glass transition takes place: the liquid freezes into an amorphous solid with no abrupt discontinuity in volume. This glassy state is not an equilibrium state and there can exist infinite different glassy states depending on the cooling rate. The amorphous solid thus produced have more free volume than the corresponding crystal. This free volume can play an important role in possible annealing of the glass. The glass transition temperature $T_g$ is not as sharply defined as $T_f$; $T_g$ shifts downward slightly when the cooling rate is reduced. The reason for this phenomenon is the steep temperature dependence of the molecular response time. When the
temperature is lowered below $T_g$, the response time for molecular rearrangement becomes larger, therefore liquidlike mobility disappears and the atomic configuration becomes frozen into a set of fixed positions to which the atoms are tied [4]. Thus, to obtain a glass it is necessary to bypass the undercooled liquid phase where it is still possible the nucleation of crystals. Below $T_g$ it can not happen.

Thermodynamic transitions are classified as being of first or second order. In a first-order transition there is a transfer of heat between the system and surroundings and the system undergoes an abrupt volume change. In a second-order transition, there is no transfer of heat, but the heat capacity does change. The volume changes and the motion of atoms increases. For example, melting is a first order transition: the phase below $T_f$ is an ordered crystalline solid while the one above $T_f$ is a disordered melt. The liquid freezes at $T_f$ into a crystalline solid, with an abrupt discontinuity in volume. But it is not clear if the glass transition can be considered a true second order phase transition. It is known that the phase below $T_g$ is a disordered amorphous solid with immobile atoms or molecules, while above $T_g$ it is a disordered amorphous solid in which atoms or molecules can wiggle around. The liquid freezes into an amorphous solid with no abrupt discontinuity in volume.

Conventional metallic glasses are obtained with a cooling rate of $10^5 \text{–} 10^6 \text{ K s}^{-1}$, thus avoiding crystallization. The result is an amorphous material that presents a short range order (SRO) but no long range order (LRO).

Nowadays many different techniques can be used to obtain this kind of materials. Probably the most famous is the melt spinner technique where the molten alloy is quenched by a rotary cooled wheel. It consists in injecting the molten materials above a wheel that rotates at high speed to make cool the alloy in a very rapidly way, like in Fig. 2.3.
Fig. 2.3 Melt-spinning technique. When the molten alloy is injected above the rotary cooled wheel, a ribbon is produced.

The glass forming ability (GFA) of a material mainly depends on a parameter related with the cooling rate of the material and by a thermodynamic law related with the material stability.

For a metallic glass the cooling rate for the glass formation is quite high, and it is an important parameter for the production. This cooling rate is related with the viscosity (that is inversely proportional to the specific volume) of the liquid, because the cooler the liquid is the more viscous is until the mobility of the atoms is considered null, and then the liquid is converted into a glass [5].

In thermodynamics, the parameter that measures the glass stability is the Gibbs free energy ($G$), that depends on the internal energy $U$ of the material and on their atomic disorder:

$$G = U + PV - TS = H - TS$$  \hspace{1cm} (2.1)

where $H$ is the enthalpy, $T$ the temperature, $P$ the pressure, $V$ the volume and $S$ the entropy.

At constant pressure the materials tend to be at a state of minimum Gibbs free energy and, consequently, the states with less $G$ are more stable. For example the most stable state of a material in the region above $T_f$ is the liquid, while if the material is in the range of temperature under $T_f$ the most stable state is the crystal. It has to be considered that the entropy, that measures the atomic “disorder”, is higher in a liquid than in a crystal. In this way, the greater is the difference between the $G$ of the liquid and the crystal, the easier is the glass formation and the frequency of nucleation is reduced.

The GFA in MGs tends to increase as more components are added to the alloy, that is the so called “confusion principle” which implies the largest number of components in an alloy system destabilizes competing crystalline phase which may form during cooling. To achieve the formation of amorphous structures even during a slow cooling, Inoue proposed three empirical rules [6]:

1) the alloy has to be made of three or more components, increasing the complexity and size of the crystal unit cell and reducing the energetic advantage of forming an ordered structure of longer range periodicity than atomic interaction;
2) the atomic radius of the principal components has to be significantly different (over 12%), to achieve high packing density and smaller free volume in the liquid state;

3) the combination of components should have negative heat of mixing between the principal components increasing the energy barrier at the liquid-solid interface and decreasing atomic diffusivity so that the elements can mix between them; this retards local atomic rearrangement and the crystal nucleation rate, extending the supercooled liquid temperature range and prolonging the time the molten metal stays in the undercooled state.

These rules are obtained experimentally. Nevertheless they can be understood in the following way: to rise the GFA, the first two rules have the aim to suppress the nucleation and the formation of the primary crystal upon solidification while the last point, related to the stability, is necessary to find elements that reduce the heterogeneous nucleation sites.

Moreover, a composition with a deep eutectic forms a liquid that is stable at relatively low temperatures and among them high GFA alloys can be found. In this way it is easier to cool rapidly until \( T_g \) because the temperature gap is smaller.

The ability to form a glass by cooling from an equilibrium liquid is equivalent to suppressing crystallization within the undercooled liquid. If the steady-state nucleation is assumed, the nucleation rate is determined by the product of a thermodynamic and a kinetic factor:

\[
I = AD \exp \left( -\frac{\Delta G^*}{k_B T} \right)
\]  

(2.2)

where \( A \) is a constant, \( k_B \) the Boltzmann’s constant, \( T \) the absolute temperature, \( D \) the effective diffusivity and \( \Delta G^* \) the activation energy which must be overcome for the formation of stable nuclei. From classical nucleation, \( \Delta G^* \) can be expressed as \( \Delta G^* = \frac{16\pi\sigma^3}{3(D\Delta G_{i,s})^2} \), where \( \sigma \) is the interfacial energy between the nuclei and the liquid phase, and \( \Delta G_{i,s} = G_i - G_s \) is the free-energy difference between the liquid state, \( G_i \), and crystalline state, \( G_s \). \( \Delta G_{i,s} \) is therefore the driving force for crystallization.

MGs exhibit a low driving force for crystallization in the undercooled liquid. The low driving force results in low nucleation rates and therefore an improved GFA. It has been found that high GFA is favored by small values of \( \Delta G_{i,s} \), which can be calculated by integrating the specific heat capacity difference \( \Delta C_{p,i,s} (T) \) according to the equation:

\[
\Delta G_{i,s}(T) = \Delta H_f - \Delta S_f T_0 - \int_T^{T_0} \left( \Delta C_{p,i} (T) - \Delta C_{p,s} (T) \right) dT + \int_T^{T_0} \frac{\Delta C_{p,i,s} (T)}{T} dT
\]  

(2.3)

where \( \Delta H_f \) and \( \Delta S_f \) are the enthalpy and entropy of fusion respectively and \( T_0 \) is the temperature at which the crystal and the liquid are in equilibrium. Low \( \Delta G_{i,s} \) means a small enthalpy of fusion \( \Delta H_f \) and a large entropy of fusion \( \Delta S_f \). The large \( \Delta S_f \) is expected to be associated with multicomponent alloys because \( \Delta S_f \) is proportional to the number of microscopic states. The increase in the number
of alloy components leads to the increase in $\Delta S_f$ and causes the increase in the degree of dense random packing in the liquid state. This is favorable for the decrease in $\Delta H_f$ and the solid/liquid interfacial energy. The real Gibbs free-energy difference becomes smaller due to the relative stabilization of the undercooled melt on cooling. The stabilization is attributed to the increasing specific heat capacity which arises from a decreasing free volume, and probably a gradual gain of short-range order in the alloy melt. The relatively small Gibbs free-energy difference is considered to be a contributing factor in the high GFA of the alloy.

Besides the thermodynamic factor (driving force), another crucial parameter for understanding GFA is the viscosity or diffusivity (kinetic factor), that is, the possibility of movement inside the liquid state: the higher is the viscosity, the more probable is the glass formation. It is a significant influence on the GFA of an alloy system, because low mobility hinders crystal nucleation. From different liquids different glasses can be formed, more or less ductile or fragile. The viscosity behavior near the glass transition classify MGs as strong liquid.

There are some coefficients used to estimate the GFA of an alloy, like the reduced temperature $T_{rg}$ that is the ratio between $T_g$ and $T_l$ where $T_l$ is the liquidus temperature. Experimentally, it has been observed that a good GFA implies values of $T_{rg}$ equal or higher than 0.6. If the liquid becomes very sluggish in crystallization within laboratory time scale and can crystallize within a very narrow temperature range. Such liquids can thus be undercooled at a low cooling rate into the glassy state [3]. Another extensively used parameter for GFA is $\Delta T_x = T_x - T_g$, which is equal to the difference between the onset temperature of the first crystallization peak ($T_x$) and the glass transition temperature, even if the comparison of GFA based on $\Delta T_x$ and $T_{rg}$ do show significant discrepancies in some alloy systems.

Summarizing, the formation mechanism and the main factors influencing the GFA have not been clearly elucidated yet. Also, the internal structure (configuration factor) of these materials is not clear, therefore it is interesting to study it to relate it with the GFA and to better understand the properties of these materials. This will allow to have a further parameter to choose the proper composition of a metallic glass.

### 2.3 Properties of metallic glasses

The amorphous state which does not possess a long range atomic order or grain boundaries as the crystalline state originated many investigations, first on structural aspects, and then on thermodynamic, mechanical and magnetic properties. The properties of MGs are thus, expected to be different than those of the alloys from which they are made. Metallic glasses (MGs) exhibit a high hardness and toughness, low fragility and resistance to plastic deformation (larger reversible elastic deformation), and frequently their electrical conductivity, magnetic susceptibility, and resistance to corrosion are superior than those of the alloys from which they are made. The mechanical properties of metallic glasses are different from the ones of conventional metals [3]. Amorphous metals derive their strength directly from their non-crystalline structure, which does not have any conventional defects, such as dislocations, on which is based the mechanism of plastic deformation and that limits the strength of crystalline alloys. The mechanism of plastic
deformation of MGs is not totally defined but it is thought to be based on shear bands that have a certain viscosity that appears like a consequence of the temperature increase experienced after the stress application. This mechanism enables a larger capacity of energy storage, that is, a higher elastic limit, but it has a lower plastic limit than the one of the same crystalline metal. Therefore, MGs have good properties in the elastic region. However, metallic glasses at room temperature are not very ductile and tend to fail suddenly when loaded in tension, which limits the material applicability in reliability-critical applications. Instead they usually are hard and less susceptible to chemical attack and corrosion. This set of properties makes this materials suitable for pieces subdued at constant rubbing or impacts. Thus, MGs can be used in applications where impact resistance and mechanical strength are important. Up to now, most fundamental studies on MGs were developed on thin ribbons and wires.

The atomic-scale disorder present in metallic glass causes its electrical conductivity to be lower than the conductivity of the corresponding crystalline metal, because the structural disorder impedes the motion of the mobile electrons that make up the electrical current. For a similar reason, the thermal conductivity of an insulating glass is lower than that of the corresponding crystalline insulator.

From a magnetic point of view, the most interesting property is that MGs are often soft magnetic materials. This property is related with the fact that the magnetic domains of the material change their orientation. The easier the change is, the smaller the area of the hysteresis loop is. MGs are easily magnetized by small magnetic fields, therefore there are less coercive and energetic losses when the polarity of the applied field is changed. MGs can be used in the production of transformers nucleus and capsule for magnetic recording.

The last property of the MGs is better resistance to wear and corrosion, because of the absence of grain boundaries, and it show a tendency to increase with the increase of the GFA, because the better is the GFA, the more compact is the structure of the glass.
CHAPTER 3. EXPERIMENTAL TECHNIQUES

3.1 Arc Melter

3.1.1 Definition

The arc melter is a furnace that allows the melting of several materials through the generation of an electric arc in an inert atmosphere, for example in Argon. The arc consists of an electric discharge (plasma) produced by the dielectric breakdown caused by a very high potential difference between two electrodes in the low pressure Ar atmosphere (pressure around 500 mbar). During the discharge process, a very intense light and heat emanation are produced so the temperature can reach very high values, thus allowing the melting of different materials, including metallic materials.

![Fig. 3.1](image)

Fig. 3.1 The arc melter.

The arc is generated by two tungsten tips that act as electrodes: one of 4mm $\varnothing$ located in the copper crucible that is used to generate the first spark of the arc in contact with the second tip of 2.4mm $\varnothing$ that is also used to maintain the arc all over the material until it is melted. This second tip is mounted in a mobile arm, thus allowing the homogenization of the melt.
In the copper crucible there are two holes of different sizes: the big one is where the metals to be melt are placed and the other one is necessary to place titanium. That is necessary to capture the oxygen that could remain inside the furnace and can cause the oxidation of the samples. While the arc melting is working it is necessary to refrigerate the copper crucible and the arm independently. The refrigerant liquid is water contained in a tank that flows into the arc melting with the help of a small water pump that gives the sufficient pressure to overcome the difference in height level and to maintain a good refrigeration flow.

A current generator yields the required potential difference between the electrodes and it is controlled by a pedal for switching on and off the current and by a knob for controlling the intensity (0-160A). Before starting to work with the arc melting, it is necessary to make the vacuum inside the furnace with a rotatory vacuum pump that reach vacuum levels of the order of $10^{-3}$ mbar. Moreover, the junctions between the different components are lubricated with an specific high vacuum grease.

The working pressure is controlled by a valve connected to an Argon tank that regulates the gas flow. A digital vacuum gauge controls the pressure inside the arc melter.
3.1.2 Procedure

The first thing to do is to prepare the samples according to the composition decided previously. This can be done with the use of a diamond circular saw suitable for cutting various kinds of materials or with a manual saw. The quantity of metals is weighted with a digital precision balance with a resolution of $10^{-4}$ g, thus resulting in an experimental error that does not exceed the 1% of the theoretical value.

![Diamond circular saw](image)

**Fig. 3.4** Diamond circular saw.

The interior of the arc melter is cleaned with acetone and alcohol to eliminate the dust or other particles that could contaminate the atmosphere. When it is cleaned, all the pieces of metals are placed in the bigger hole of the copper crucible; the tungsten tip of 2.4mm $\varnothing$ is fixed at the mobile arm with the Allen key of 1.5, so that its length is between 8 and 13mm. After that the arc melter can be closed with a transparent glass allowing the visual control of the melting process.

The next step consists in establishing the working pressure inside the arc melter, usually between 400 and 500 mbar. The desired vacuum pressure is reached by turning on the rotatory pump and opening the valve connected with the furnace. To ensure a pure atmosphere several purges must be done, i.e., when the vacuum gauge signals a pressure of about $2 \times 10^{-1}$ mbar, the valve connected with the pump is closed and Ar is injected up to 500 mbar. Then, the valve connecting with the rotatory pump is opened again and the process is repeated.

Just before the melting, the vacuum pump is turned off and the water one is turned on to refrigerate the circuit; once the current source is connected and fixed at an initial intensity value of 40A, the plasma arc is created by approaching the two tungsten tips. Once the arc is formed it is necessary the use of welding masks to protect the eyes from the radiation. The arc is directed towards the sample and the melting process begins. It could be necessary to repeat this procedure several times with different current intensities to ensure a complete melting of the sample.
When this procedure is complete, an homogeneous bulk of the desired alloy is formed. At this point, it is convenient to weight the sample to check the possible lost of materials (specially if the materials are used as powder). The last thing to do is to clean all the parts of the furnace with acetone and alcohol. Moreover the tungsten tip in the mobile arm must be changed before the next use because it became round due to the high temperature reached during the melting.

### 3.2 Melt Spinner

#### 3.2.1 Definition

The rapid solidification system with a copper wheel (*melt-spinner*) is a device that permits the production of amorphous metallic ribbons from a molten alloys. The sample is introduced in a quartz crucible with a small hole at its end to allow the evacuation of the molten material over the spinning wheel. The crucible is introduced in an induction coil through which a fixed current flows, thus creating a magnetic field that induces the creation of Focault currents (also known as eddy currents). The Joule effect produced by these eddy currents raises the temperature high enough to melt the sample. Therefore, the melt spinner technique can only be used with alloys with metallic constituents. In this way, the sample can be heated over the melting point and then, by the application of an overpressure inside the crucible, the liquid alloy can be injected through the hole of the crucible impacting against the spinning copper wheel while it is rotating. Due to the high thermal conductivity of Cu and the high lineal velocity of the wheel (up to 65 m/s) the liquid can be cooled in a very fast rate (about $10^6$ K/s). Thus, the atoms can not reorganize themselves in its equilibrium position before the temperature is further reduced and then an amorphous material without any crystalline order can be obtained. This process takes place in a chamber with an Argon atmosphere typically of 500mbar after purging the chamber several times.
3.2.2 Components

The main components of the melt spinner are the copper wheel and the induction coil, that are described next.

A) Copper wheel:
The most important part of the melt spinner is the copper wheel with a diameter of 20cm that allows the ultrafast cooling of the melted materials obtaining metallic ribbons that have an amorphous structure. Every time the wheel is used it must be cleaned in order to not contaminate the new samples with other materials or damage the surface of the ribbon.

The control of the wheel speed is made by a potentiometer that have a scale expressed in unknown unities for which the speed of the wheel can be between 0 and 1000, but, of course, this does not give any information about the real speed. For this reason the speed of the wheel was measured with a digital tachometer that is an instrument that measures the rotation speed of a shaft or disk, as in a motor or other machines. The tachometer usually displays the angular velocity in revolutions per minute (RPM) and the linear speed is calculated as follows:
\[
\text{speed} = \frac{\text{Measure} \cdot 2 \cdot \pi \cdot R}{60 \cdot 1000} \quad (3.2.1)
\]

where \( R \) is the radius of the wheel in millimeters.

So, with measures at different units of the potentiometer, a table can be obtained in order to known the correspondent lineal speed for the principal units. Any other value can be linearly interpolated using the following relation:

\[
\text{Wheel speed} = \frac{\text{Lecture} - B}{A}
\]

\[
A = 14,737 \text{ s/m} \quad B = 56,548
\]

It is necessary to say that the application range of this formula is between 3 and 64 m\(\cdot\)s\(^{-1}\).

<table>
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<td>650</td>
</tr>
<tr>
<td>44.07</td>
<td>700</td>
</tr>
<tr>
<td>47.19</td>
<td>750</td>
</tr>
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</tr>
<tr>
<td>57.05</td>
<td>900</td>
</tr>
<tr>
<td>60.14</td>
<td>950</td>
</tr>
<tr>
<td>63.24</td>
<td>1000</td>
</tr>
</tbody>
</table>

**Tab. 3.1** Correspondence between the potentiometer value and the speed of the wheel.

**B) Induction coil:**
Both the copper wheel and the copper induction coil are located inside a steel high vacuum chamber. As explained before, the electric current flows in the coil allows the melting of the sample through the generation of eddy currents in the material. It must be remarked that there is a water flux inside the coil to refrigerate it and thus, avoiding its melting. The induction oven allows to control the way the electric current flow with two different options:
• fixing the intensity and controlling the application time with a pedal;
• fixing the time during which the device applies the desired intensity.

It is necessary to avoid the contact between the sample and the coil, otherwise the furnace does not work because it would interpret it like a shortcircuit. Moreover it is able to calculate the resonance frequency thanks to the calculation of the impedance of the coil and of the sample. The frequency range is between 200 kHz and 300 kHz. If suddenly during the work the frequency exceeds these limits or changes rapidly, it stops automatically. This usually happens when there is the sample injection.

![Fig. 3.8 The coil above the wheel through which the current flows and inside which the sample is located.](image)

*C) Auxiliar components:*
Once the sample is melted it does not fall over the wheel through the hole in the crucible due to the superficial tension. Thus, to inject the sample, an overpressure with respect the chamber pressure is needed inside the crucible. The Argon that is used for the injection in contained in two deposits that can support pressures from 1 bar to 10 bar. For this work the pressures needed are between 0.5 and 1 bar.

![Fig. 3.9 Deposits.](image)
There are other auxiliary components, like the refrigeration circuit that is composed by a distilled water container and a water pump. This is very important because it has the role to refrigerate the induction coil and the high vacuum pump. The temperature of the water has to be lower than 25 ºC.

Another important component is the vacuum circuit composed by a rotatory pump and an high vacuum turbomolecular pump. This system allows to make the vacuum inside the chamber in order to remove all the impurities before setting the Ar atmosphere. The first step is to obtain a vacuum pressure of about $10^{-3}$ mbar with the rotatory pump, then the high vacuum pump can start to work and it can reach a pressure of $10^{-10}$ mbar. In the present case it is enough a pressure of $10^{-5}$ mbar because of the purity of the used Argon.

![Vacuum circuit: at the left, the vacuum pump; at the right, the high vacuum pump.](image)

The flow of Argon used to fill the chamber and the deposits is controlled by several valves connected with the melt spinner. The Ar pressure desired is measured by an analogical manometer that has a range of measure between 0 mbar and 1000 mbar. Usually, the work pressure in the chamber is offset to 500 mbar, while inside the deposits the Ar pressure is set to 1000 mbar so that there is enough difference in the pressure to make the injection. However, the vacuum pressure is measured with two digital vacuum gauges with different range of measure to get a precise value at low pressures.

<table>
<thead>
<tr>
<th>Manometer</th>
<th>Range of measure (mbar)</th>
<th>Resolution (mbar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chamber</td>
<td>0 – 1000</td>
<td>20</td>
</tr>
<tr>
<td>Deposits</td>
<td>0 – 1000</td>
<td>20</td>
</tr>
</tbody>
</table>

**Tab. 3.2 Characteristics of the analogical manometers.**

<table>
<thead>
<tr>
<th>Gauge</th>
<th>Range of measure (mbar)</th>
<th>Precision (mbar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TTR91</td>
<td>$5 \cdot 10^4 – 1000$</td>
<td>$10^{-3} – 100$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\pm 15%$ measure</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$5 \cdot 10^{-7} – 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\pm 50%$ measure</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$100 – 1000$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\pm 50%$ measure</td>
</tr>
<tr>
<td>PTR225</td>
<td>$10^{-9} – 10^{-2}$</td>
<td>$10^{-8} – 10^{-8}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\pm 30%$ measure</td>
</tr>
</tbody>
</table>

**Tab. 3.3 Characteristics of the digital vacuum gauges.**
3.2.3 Procedure

After the production of the bulk alloy in the arc melter it is placed inside the crucible and located inside the melt spinner chamber. To do that, in the upper part of the crucible a Teflon ring is fixed in order that it can be hold in the copper support that then it is screwed in the upper part of the vacuum chamber (see Fig. 3.11). After this, the copper support with the crucible is lowered until all the material is contained inside the induction coil and the distance between the crucible’s hole and the wheel is between 1 mm and 2 mm. Now it is possible to close the door of the chamber to make the vacuum inside.

![Fig. 3.11 Location of the crucible at the support inside the vacuum chamber. At the left, the crucible before to be located inside the coil. At the right, the crucible at a distance of 1 mm from the wheel.](image)

The first vacuum is obtained with the rotatory pump, followed by the high vacuum pump that can be used to obtain a pressure of \(10^{-6}\) mbar. The removal of the oxygen from the chamber is necessary to avoid the oxidation of the metals during the melting process. Now it is possible to fill the chamber with the Ar atmosphere that will be used during the work, i.e., about 400/500 mbar. The deposits also have to be filled with Ar with a pressure that can vary from 600 to 1000 mbar for the injection. After this, the wheel can be switched on choosing a particular speed (usually it is \(40\) m\(\cdot\)s\(^{-1}\)) and it is also necessary to switch on the refrigeration circuit to not damage the turbomolecular pump and the induction coil.

At that moment, the induction oven can be switched on and proceed to melt the sample and inject it on the spinning wheel. Thus, some amorphous ribbons are produced.
3.2.4 Melt spinner protocol

Summarizing, the procedure that must be done to produce ribbons from the bulks melted in the arc melter, is the following:

1) Preparing the chamber
   a) Check the melt-spinner state.
   b) If the chamber is in vacuum fill the chamber with air opening the venting valve.
   c) Put on the gloves before touching anything.
   d) Put the crucible with the sample in the induction oven.
   e) Adjust the crucible-wheel distance.
   f) Close both chamber doors.

2) Primary vacuum
   a) Open the red valve
   b) Open guillotine valve
   c) Open the valves between the chamber, crucible and deposits to ensure that the pressure is the same
   d) Close the venting valve
   e) Switch on the rotatory pump
   f) Wait until the chamber pressure goes below $10^{-1}$ mbar

3) High vacuum
   a) Switch on the water pump. Open the valve for turbomolecular pump refrigeration.
   b) Close red valve connected with the rotary pump
   c) Switch on the turbomolecular pump.
   d) Open the guillotine valve (if closed).
   e) Wait until $P < 10^{-5}$ mbar
   f) Close the guillotine valve connected with turbomolecular pump
   g) Close the valve for turbomolecular pump refrigeration
   h) Switch off turbomolecular pump.
   i) Switch off the rotatory pump.

4) Start the wheel switching on.

5) Filling the chamber with Argon controlling the pressure with the proper valve.

6) Filling the deposits with the desired injection pressure of Argon controlling it with the proper valve.

7) Making the ribbon
   a) Start induction oven refrigeration
   b) Switch on the induction oven
   c) Melt the sample with the black pedal
   d) Eject the sample to produce the ribbons injecting Argon.

8) Stopping the system
   a) Stop the wheel
   b) Switch off the water pump
   c) Open the red valve
   d) Open the venting valve
   e) Open the chamber doors when the atmospheric pressure is reached
   f) Collect the ribbons
   g) Clean chamber and wheel.
3.3 Mössbauer Spectroscopy Technique (TMS)

In 1957, R.L. Mössbauer made the observation of recoilless nuclear resonant absorption, that is, if the emitting and absorbing nuclei are bound in a solid, a certain fraction of gamma rays ($\gamma$) are emitted and absorbed with negligible energy loss due to recoil. This can be understood considering that the nucleus is rigidly bound to the solid in a way that the recoil is taken up by the entire solid.

Mössbauer spectroscopy is a technique with a very high resolution in energy achieved with recoil-free gamma rays, based on the Mössbauer effect that is based on the fact that the recoil is taken up by the crystal as a whole and not by an individual atom. This makes the recoil energy immeasurably small and puts the emission and absorption processes back in step. The recoilless absorption of the gamma-rays results in a spectroscopy having the resolution of the lifetime uncertainty of the excited nuclear state, about $10^{-8}$ eV. Usually, this resolution is good enough to resolve the so-called hyperfine energy-splitting of the nuclear levels caused by electric or magnetic fields. Often, the hyperfine energy levels are scanned by moving a radioactive source repetitively toward and away from an absorber. Through the Doppler shift, this varies the energy of the gamma-rays arriving at the absorber. The Mössbauer effect is of fundamental importance because it provides a means of measuring some of the weak interactions between the nucleus and its surrounding nuclei and electrons thus allowing to get information about the short range order of the studied materials being crystalline or amorphous.

3.3.1 Mössbauer effect

The Mössbauer effect is a particular process of a resonant absorption. It involves two identical radioactive isotopes, one in a excited state of energy $E_x$ and the other in the ground state of energy $E_0$. The excited isotope decays with a resonant transition to the ground state with the emission of a gamma photon ($\gamma$) of energy $\Delta E = E_x - E_0$ that can be absorbed by the isotope in the ground state. After the resonant absorption of the $\gamma$ ray, the second isotope remains in the excited state for a lifetime $\tau$ and afterwards it decays to the ground state with another emission of a $\gamma$ ray or with an inner conversion.

During the process of emission of a $\gamma$ ray by a nucleus, a certain amount of the excitation energy (the recoil energy $E_R$) is given to the nucleus in order to conserve momentum. Thus, the energy of the emitted $\gamma$ ray $E_\gamma$ is reduced by the same amount:

$$E_\gamma = \Delta E - E_R = \Delta E - \frac{\Delta E^2}{2Mc^2}, \quad (3.3.1)$$

where $p$ is the momentum of the gamma photon, $M$ is the mass of the emitting nucleus and $c$ the velocity of light. In the case of high-energy nuclear radiation, the recoil energy is much larger than the width of the absorption line and, therefore, the probability of the nuclear resonant absorption is greatly reduced because of the energy loss due to the recoil effect.
Moreover, the possible movement of the isotope must be also considered. If an isolated nucleus of mass \( M \) moves with a velocity \( V \) along the direction in which the \( \gamma \)-rays are to be emitted, his energy above the ground state is \( E_\theta + \frac{1}{2}MV^2 \). After the emission of the \( \gamma \)-ray with energy \( E_\gamma \), the nucleus recoils and has a new velocity \( V + v \) and a total energy of \( \frac{1}{2}M(V + v)^2 \). Therefore, the actual energy of the emitted photon is given by

\[
E_\gamma = \Delta E - \frac{1}{2}MV^2 - MvV = \Delta E - E_R - E_D
\]

The \( \gamma \)-ray is thus deficient in energy by a recoil energy \( E_R \) which is independent of the initial velocity \( V \), and by an energy \( E_D \) that depends on the initial velocity \( V \) (therefore it can be positive or negative) and that is usually known as a Doppler energy.

Considering that the Doppler energy \( E_D \) is also dependent on the random thermal motion of the nucleus, a mean value of \( \overline{E_D} \) can be defined related to the mean kinetic energy per translation degree of freedom, \( E_k = \frac{1}{2} k_B T \), by

\[
\overline{E_D} = 2\sqrt{\overline{E_kE_R}} = E_\gamma \sqrt{\frac{2E_k}{Mc^2}}
\]

where \( k_B \) is the Boltzmann’s constant and \( T \) is the absolute temperature.

As a result, the statistical energy distribution of the emitted \( \gamma \)-ray is displaced from the true excited state energy by \( -E_R \) and broadened by \( E_D \) into a Lorentzian distribution of width \( 2E_D \), as shown in Fig. 3.3.1. The distribution for the absorption has the same profile but displaced by \( + E_R \). The overlap zone is the possible range of energies in which the Mössbauer effect can be obtained to produce a resonant signal. Thus, nuclear resonant absorption will only have a significant probability of occurrence if the emission and absorption energy distributions strongly overlap, even if in reality it is extremely small.

![Fig. 3.3.1](image_url)

*Fig. 3.3.1 The statistical distribution in the \( \gamma \)-ray energy for the resonant overlap of the successive emission and absorption events.*
A recoil-free emission and absorption of a nuclear $\gamma$-ray can be observed in solids because the Mössbauer nucleus is locked into a crystal or a metallic matrix such that it can take up the recoil momentum and absorb the recoil energy on emission or absorption of a $\gamma$-ray is as a whole. In fact the Mössbauer effect provides a means of eliminating the destructive effects of the recoil and thermal energy, because the behavior of the recoiling nucleus is different when it is isolated or instead it is fixed in a crystal lattice. The energy loss due to the recoil and the possible energy exchange between the nucleus and the matrix in which it is embedded are governed by the dynamic of the crystalline solid. The recoil momentum is transferred to the lattice and the recoil energy can induce a lattice-vibration phonon excitation. As the phonon energies are quantized, the recoil energy can only be transferred to the matrix if it corresponds to an allowed quantum jump.

The model for the vibrational modes of a crystal lattice is described by quantum mechanics by the mathematical model of Einstein solid with only one vibrational frequency: the transfer of energy to the lattice can only take place in integral multiples of $\hbar\omega$, where $\omega$ is the vibrational frequency. If the recoil energy $E_R$ is less than $\hbar\omega$, either zero or one unit of vibrational energy can be transferred to the lattice causing a mismatch in energies. The probability of a resonant emission or absorption without energy exchange with the lattice is known as "factor $f$", that is $f$ is the measure of the probability of occurrence of the Mössbauer effect in a nuclear transition. The average energy transferred is equal to $E_R$. If a fraction $f$ of the emission events results in no transfer of energy to the lattice (zero-phonon transition) and a fraction $(1-f)$ transfers one phonon of energy $\hbar\omega$, then

$$E_R = (1-f)\hbar\omega$$

In a zero-phonon emission, the whole crystal rather than a single nucleus recoils, being the recoil energy and the Doppler broadening very small because they contain the reciprocal mass $1/M$ and much less than $\Gamma$, the full width at half maximum (FWHM) of the Lorentzian spectral line:

$$I(E)dE = \frac{I_0(\Gamma/2\pi)}{(E-E_0)^2 + (\Gamma/2)^2} dE$$

where $E_0$ is the central energy of the line and $I(E)$ determines the emitted energy between $E$ and $E + dE$. A recoil-free nuclear decay yields a $\gamma$ ray with a very narrow linewidth or energy distribution. The natural width of the line ($\Gamma$) only depends on the mean lifetime, $\tau = t_{1/2}/\ln 2$, of the nuclear excited state which generates the $\gamma$ ray, and it is controlled by the Heisenberg uncertainty principle: $\Gamma\tau \geq \hbar$ ( $\hbar = 2\pi\hbar$ is the Planck's constant). In the case of $^{57}\text{Fe}$ the transition of $E_0 = 14.4$ keV has a FWHM of $\Gamma = 4.67 \times 10^{-9}$ eV.

Therefore, as $\Gamma$ is so narrow the factor $f$ must be as large as possible to reduce the energy loss due to the recoil. It is the recoilless or recoil-free fraction.

In the framework of the Debye model, which embodies a continuum of vibrational frequencies in the harmonic oscillator approximation, the parameter $f$ can be written as:
\[ f = \exp \left\{ -\frac{6E_g}{k \theta_D} \left[ \frac{1}{4} + \left( \frac{T}{\theta_D} \right)^2 \int_0^\infty \frac{x}{e^x - 1} \, dx \right] \right\} \quad (3.3.6) \]

where \( k_B \) is the Boltzmann’s constant and \( \theta_D \) is the Debye temperature, that is, the temperature associated with the maximum frequency of the excited phonon in the absorber, so that \( \hbar \omega_{\text{max}} = k_B \theta_D \).

From this equation the following things can be observed:

i) \( f \) increases when temperature \( T \) decreases;

ii) to give an acceptable recoil-free fraction \( f \) the element must have a high Debye temperature \( \theta_D \), that is, to place the atom in a rigid lattice;

iii) \( f \) decreases rapidly with the increase of the photon energy associated with the transition.

To observe the Mössbauer effect it is not enough to have a significant factor \( f \), it is also necessary that the emitted energy coincides with a possible nuclear transition of the absorbing nucleus. Thus, the resonance can be destroyed if the chemical or structural environments of the two nucleus are different because the nuclear levels can be perturbed by electric and/or magnetic interactions between the nucleus and its environment. To tune the energy of the source with the possible energy levels in the absorber, an appropriate velocity must be applied to the source relative to the absorber. In that way, the Doppler effect can be used to change the energy of the \( \gamma \)-ray, increasing or decreasing the energy of the emitted \( \gamma \) photon to obtain the resonance condition:

\[ E(v) = E_0 (1 + v/c) \quad (3.3.7) \]

where \( v \) is the relative velocity between source and absorber and \( c \) the speed of light.

The resulting nuclear gamma resonant spectroscopy, the Mössbauer spectroscopy, can be used to study a variety of phenomena producing shifts and splittings of the nuclear energy levels.

### 3.3.2 The set-up of the Mössbauer spectroscopy

The most usual experimental arrangement for the Mössbauer spectroscopy involves a radioactive source containing the Mössbauer isotope in an excited state and an absorber consisting of the material to be investigated which contains the same isotope in its ground state. The study of the Mössbauer effect in \(^{57}\)Fe has been very fruitful because of the narrow natural linewidth of the 14.4 keV transition. This transition is characterized by a lifetime \( \tau \approx 10^{-7} \) s and a linewidth \( \Gamma = \hbar / \tau \approx 10^{-8} \) eV. The emission source of \(^{57}\)Fe Mössbauer spectroscopy is usually \(^{57}\)Co (embedded in a solid metallic matrix) which undergoes a spontaneous electron capture transition to give a metastable state of \(^{57}\)Fe which in turn decays to the ground state via a \( \gamma \) ray cascade which includes the 14.4 keV Mössbauer \( \gamma \)-ray. Fig. 3.3.1 shows the nuclear decay scheme for Mössbauer resonance in \(^{57}\)Co.
$^{57}$Co decays to $^{57}$Fe with a half life of about 270 days from a level with a nuclear angular momentum $m_z = 5/2$ and $E=136$ keV by electron capture (EC). The 91% of the decays of this level results in the excitation of the 14.4 keV level with $\tau \approx 1.4 \times 10^{-7}$ s. However, because the conversion coefficient $\alpha$ is about 9, the 90.2% of the decays of this levels occurs by electron conversion and only the 9.8% of the decays of this level result in the emission of a $\gamma$ photon with the energy of 14.41 keV. The natural width of the $3/2 \rightarrow 1/2$ transition allow to resolve the hyperfine interactions and gives appreciable values of the factor $f$ at room temperature.

![Diagram](image)

**Fig. 3.3.2** The nuclear decay scheme of a $^{57}$Co source leading to $\gamma$-ray emission.

The radioactive source nuclei are usually embedded in a matrix which provides the necessary solid environment as well as the simplest possible hyperfine interaction between the nuclei and their environment. In order to investigate the energy levels of the Mössbauer nucleus in the absorber it is necessary to modify the correct energy for resonant absorption moving the source relative to a stationary absorber, and hence giving to the $\gamma$-ray an energy shift due to the Doppler effect. The motion of the source is usually oscillatory in order to provide a continuous energy scan. The required velocity is of a few mm/s.

Resonant absorption occurs when the energy of the emitted photon by $^{57}$Co just matches the nuclear transition energy for a Mössbauer nucleus in the absorber. The measurement of a Mössbauer spectrum is almost exclusively carried out by repetitively scanning the whole velocity range required, accumulating the whole spectrum and allowing a continuous monitoring of the resolution. This can be achieved electro-mechanically, and a typical Mössbauer spectrometer is illustrated schematically in **Fig. 3.3.2**.
The major component is the Data Acquisition System that is a multichannel analyzer which can store an the total number of \( \gamma \)-counts, using binary memory storage like a computer, in one of several hundred individual registers known as channels. Each channel corresponds to a certain velocity, that is to a specific energy and it is held open in turn for a short time interval of fixed length, which is controlled by a waveform generator that is a stable constant-frequency device and that synchronously provides the motion of the source. Any \( \gamma \)-counts registered by the detection system during that time interval are added to the accumulated total already stored in the channel (photons with the same energy). The resulting Mössbauer spectrum consists of a plot of number of \( \gamma \)-rays counts against the velocity of the source with respect to the absorber, usually measured in millimeters per second, which constitutes the energy axis of this spectrum. The statistic of the random counting predicts that the standard deviation in \( N \) registered events is \( \sqrt{N} \) : thus the standard deviation in \( 10^4 \) counts is 1%, and in \( 10^6 \) counts is 0.1%of the total counts.

If emitting and absorption nuclei are identical, with a cubic environments, then the transition energies are identical and this produces a spectrum as shown in Fig. 3.3.3, that is, a single absorption line.
Fig. 3.3.4 Simplest Mössbauer spectrum obtained from emitter and absorber in identical conditions showing the velocity scale and motion of source relative to the absorber.

3.3.3 Hyperfine interactions

In addition to the intensity changes and shifts of Mössbauer spectrum due to variations in the average motion of the Mössbauer atoms, the energies of the nuclear states are influenced by changes in the electromagnetic environment surrounding the emitting or absorbing nuclei. The electromagnetic environment of a nucleus is partly determined by the electrons of the same atom and by near cations, therefore the magnetic momentum of the nucleus can interact with the electric and magnetic fields of the environment causing small changes in their nuclear energy levels. The interactions with the electromagnetic environment are considered to be hyperfine effects and can be the following ones, considered in the Mössbauer spectroscopy:

i) the electrostatic interaction between the nuclear energy levels and their surrounding electronic environment, described by the hyperfine parameter called “isomer shift” (IS or δ) which arises from the difference in s electron density in the nucleus between the source and the absorber;

ii) the electrostatic interaction between the electric field gradient caused by nearby electrons and the electric nuclear quadrupole momentum, described by the quadrupole interaction or quadrupole splitting (ΔE_Q);

iii) the magnetic interaction between the nuclear magnetic dipole momentum and a magnetic field, internal or applied, called nuclear Zeeman interaction.

The energy changes caused by these hyperfine interactions are very small, of the order of billionths of an electron volt. Such miniscule variations of the original γ-ray are quite easy to achieve by the use of the Doppler effect. Fractions of mm/s compared to the speed of light (3x10^{11} mm/s) gives the small energy shifts necessary to observe the hyperfine interactions. For convenience the energy scale of a Mössbauer spectrum is thus quoted in terms of the source velocity.
3.3.3.1 Isomer Shift (IS)

The measurement of isomer shift provides unique information regarding the nature of the chemical bond and structure of condensed systems. The isomer shift is the manifestation of the electron monopole or Coulomb interaction between the nuclear and electron charge distributions at the nucleus that has a nonzero size.

As the ns electrons have a nonzero probability density at the nucleus, the electrostatic interaction will produce a slight shift in the nuclear energy level $\Delta U$ as compared with the energy of the "bare" nucleus. This interaction may be different for the nuclear ground and excited states because these two states do not necessarily have the same volume nuclear size, $R_{gs} \neq R_{gd}$. A nucleus changes its radius by a small increment $\delta R$ during its transition from the excited state to the ground state, thus there will be a simultaneous change in the electrostatic energy given by:

$$
\Delta E = \Delta U_{ex} - \Delta U_{gd} = \frac{1}{5\epsilon_0} Z e^2 R^2 \frac{\delta R}{R} |\psi_{ns}(0)|^2
$$

where $Z$ is the nuclear charge, $|\psi_{ns}(0)|^2$ represents the electronic probability density of ns electrons at the nucleus, $\delta R = R_{ex} - R_{gd}$ and $R = (R_{ex} + R_{gd})/2$ so $\delta R/R$ represents the normalized radius difference between the nuclear excited state and the nuclear ground state.

In the Mössbauer experiment the isomer shift or chemical shift, usually denoted by the symbol $\delta$, is a direct measure of the total electron density at the nucleus in the resonant absorber relative to the source. The result is observed as the difference between the energy shift of the emitted photons $\delta F$ and of the absorbed photons $\delta A$:

$$
\delta = \delta_F - \delta_A = \frac{Z e^2 R^2}{5\epsilon_0} \frac{c}{E_Y} \left[ |\psi_{ns}(0)|^2_{source} - |\psi_{ns}(0)|^2_{absorber} \right] \frac{\delta R}{R}
$$

$\delta$ is a function of both the nuclear and electronic properties of the system. For $^{57}\text{Fe}$, $\delta R/R$ is of the order of $10^{-4}$ and is negative. The term $c/E_Y$ is necessary to relate the isomer shift with the Doppler velocity expressed in mm/s.

This situation is shown schematically in Fig. (a): the transition energy between the nuclear ground and excited states in an isolated nucleus is modified by the different electronic environments of the nucleus in the source and absorber. The application of a Doppler velocity to the source is therefore necessary to attain resonance and detect the shift in the position of the resonance line from zero velocity. When additional hyperfine interactions are present the isomer shift sets the gravity center position of the whole Mössbauer spectrum.

In the Mössbauer spectroscopy analysis, all the isomer shift values are given relative to the one of the $\alpha$-Fe phase, that is -0.1, so this point is considered like the point zero.
3.3.3.2 Electric quadrupole interaction

If the nuclei to study are not in a symmetric electronic environment, the presence of an electric field gradient (EFG) can cause a splitting of the nuclear energy levels. This EFG is usually expressed as a function of the diagonal components of the potential difference associated to the electric field, $V_{zz}$, $V_{yy}$ and $V_{xx}$. Nuclei in states with a quantum angular momentum $I>1/2$ have a non-spherical charge distribution producing a nuclear quadrupole moment that interacts with the asymmetric electronic charge distribution to give a splitting, $\Delta E_Q$, of the nuclear energy levels, partly removing the degeneracy of the nuclear spin states.

The nuclear quadrupole moment $Q$ is a measure of the deviation from spherical symmetry of the nuclear charge. It is expressed by:

$$eQ = \int \rho r^2 \left(3\cos^2 \theta - 1\right) d\tau$$

(3.3.10)

where $+e$ is the charge of the proton and $\rho$ is the charge density in the volume element $d\tau$.

The interaction of the nuclear quadrupole moment with the electronic environment is expressed by the Hamiltonian:

$$\hat{H} = -\frac{1}{6} e\hat{Q} \cdot \nabla \hat{E}$$

(3.3.11)

where $\nabla \hat{E}$ represents the electric field gradient (EFG) at the nucleus which is a symmetric tensor that can be written as:

$$\nabla_i E_j = -\frac{\partial^2 V}{\partial x_i \partial x_j} = -V_{ij}.$$  

(3.3.12)

It will always be possible to select a coordinate system such that all the $V_{ij}$ terms with $i \neq j$ are zero, leaving the three finite principal values $V_{zz}$, $V_{yy}$ and $V_{xx}$. Furthermore, the EFG trace tensor vanishes, so that:

$$V_{zz} + V_{yy} + V_{xx} = 0$$

(3.3.13)

and if the principal axes are chosen such that:

$$|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$$

(3.3.14)

it will be only necessary to specify two parameters to completely describe an electric field gradient tensor in this system:

1. $V_{zz} = eq$ is taken to be the largest value of $|V_{ij}|$ along the symmetry axis where the quantity $q$ has the dimension of the inverse of the volume;
2. an asymmetry parameter that measures the distortion from the cubic symmetry of the electron distribution around the atoms, $\eta$, defined by:
\[ \eta = \frac{|V_{xx} - V_{yy}|}{V_{zz}}, \quad 0 \leq \eta \leq 1. \] (3.3.15)

Now, the Hamiltonian operator of the quadrupole interaction in the principal axes system has now the form

\[ \hat{H} = \frac{eQV_{zz}}{4I(2I-1)} \left[ 3\hat{I}_z^2 - \hat{I}_x^2 - \hat{I}_y^2 + \frac{\eta}{2} (\hat{I}_x^2 + \hat{I}_y^2) \right] \] (3.3.16)

where \(-e\) is the electron charge, \(V_{zz}\) is the EFG in the z direction, \(Q\) is the nuclear electric quadrupole moment, \(I\) (the maximum value that can have \(m_I\)) is the nuclear quantum number of spin, \(\hat{I}\) is the nuclear spin operator, \(\hat{I}_x = \hat{I}_z \pm \hat{I}_y\) are the shift operators and \(\hat{I}_x, \hat{I}_y, \hat{I}_z\) are the operators of the nuclear spin projections onto the principal axes.

If the electric field gradient tensor has axial symmetry (\(\eta = 0\)) the energy levels, that is the eigenvalues of \(H\), are given by

\[ E_q = \frac{e^2 qQ}{4I(2I-1)} \left[ 3I_z^2 - I(I+1) \right] \] (3.3.17)

where the quantum number \(I_z\) (the nuclear magnetic spin quantum number) can take the values of \(I, I-1, ..., 1\). For example, the excited state of \(^{57}\text{Fe}\) has \(I = 3/2\) and it splits in two substates \(m_1 = \pm 1/2\) and \(m_2 = \pm 3/2\) with a change of energy with respect the unsplit state of \(-eQV_{zz}/4\) and \(+eQV_{zz}/4\), respectively.

If the symmetry is lower than axial, i.e. in general case when \(\eta > 0\), an exact expression of the eigenvalues is

\[ E_q = \frac{e^2 qQ}{4I(2I-1)} \left[ 3I_z^2 - I(I+1) \right] (1 + \frac{\eta^2}{3})^{1/2} \] (3.3.18)

with the energy levels at \(E_0(\pm 3/2) = (eQV_{zz}/4)(1 + \eta^2/3)^{1/2}\) and \(E_0(\pm 1/2) = -(eQV_{zz}/4)(1 + \eta^2/3)^{1/2}\). In the case of \(^{57}\text{Fe}\) the excited state \(I_e = 3/2\) associated with the transition \(E_\gamma = 14.4\ \text{keV}\) has a \(Q\) different from zero, while the ground state with \(I = 1/2\) has \(Q = 0\) for the symmetry of the nuclear charge. So the excited state \(I_e\) is divided into two substates while the ground state remains degenerated.

A Mössbauer transition in an policrystal absorbent with a random orientation of the crystals can take place according to the selection rule \(\Delta m_z = 0, \pm 1\). This gives two line spectrum or ‘doublet’ that represents the two possible transitions of equal intensity (asymmetry can be caused by an increasing of temperature or if the factor \(f\) is anisotropic) with a separation in energy called the quadrupole splitting \(\Delta E_0\) that in the case of the absorption lines of an \(^{57}\text{Fe}\) nucleus in the principal axis system of the EFG is
The splitting is then a function of the nuclear properties, the quadrupole moment and the electronic terms $V_{zz}$ and $\eta$.

The electric field gradient is made up of two contributions. The largest is a valence electronic term $q_{val}$, that is the asymmetry of the electronic charge distribution in the valence band ($3d$ orbitals) of the Mössbauer atom and it varies with the temperature. The second and smaller term is the lattice contribution $q_{lat}$, due to the charge of the ions around the Mössbauer atom, which is nonzero if the nucleus is in a noncubic lattice.

Iron compounds show a broad range of quadrupole interactions, which may be related to their spin-state and distortion geometry.

![Diagram](image)

**Fig. 3.3.5** Effects of (a) Isomer shift and (b) Quadrupole splitting on Mössbauer spectra. The isomer shift is the difference between the midpoint of the doublet and zero on the velocity scale.

### 3.3.3.3 Magnetic hyperfine splitting

If there is a magnetic field, internal or externally applied, its interaction with the nuclear magnetic dipole moment $\mu$ will affect the energy of the nucleus and will split the nuclear state with spin $I > 0$ into its $2I + 1$ component Zeeman states. The interaction of $\mu$ with a magnetic flux density of the hyperfine field $B_{hf}$ of electronic origin experienced by the nucleus is expressed by the Hamiltonian

$$
H = -\vec{\mu} \cdot \vec{B}_{hf} = -g \mu_N I \cdot \vec{B}_{hf}
$$

(2.3.20)

where $\mu_N$ is the nuclear magneton ($\varepsilon h / 4\pi m_p = 5.04929 \times 10^{-27} \text{ A}\cdot\text{m}^2$ or $\text{J}\cdot\text{T}^{-1}$) and $g$ is the nuclear g-factor or gyromagnetic ratio $g = \mu / (I\mu_N)$. Solving this Hamiltonian yields the energy levels of the nucleus in the field:
\[
E_m = -\frac{\mu B_{hf}}{l} m_z = -g \mu_N B_{hf} m_z
\]  

(2.3.21)

where \(m_z\), as defined before, is the magnetic quantum number representing the z-component of \(I\) and can take the values \(l, l-1, \ldots, -l\). The excited and ground states will in general have different values of \(\mu\) as well as \(I\) and both will be split by the magnetic interaction. Transition can take place between sublevels which obeys to the selection rule \(\Delta m_z = 0, \pm1\). The resultant Mössbauer spectrum contains a number of resonance lines. When an electric field gradient acts on the nucleus, small enough to be regarded as a perturbation of the magnetic interaction, the Mössbauer spectrum will not show the symmetric splitting found when \(V_{zz}\) is zero.

In the case of \(^{57}\text{Fe}\), the excited state has a spin of \(3/2\) and the ground state \(1/2\), leading to four and two sublevels, respectively. In a magnetic dipole transition, for the Mössbauer \(\gamma\)-rays of 14.4 keV, the selection rule \(\Delta m_z = 0, \pm1\) leads to six possible transition and hence a Mössbauer spectrum with six absorption lines as shown in Fig. 3.3.6. The six lines are not of equal intensity, because the transitions probability between the nuclear sublevels affect the intensities of each line and give information on the relative orientation of the magnetic field at the nucleus with respect to the direction of propagation of the \(\gamma\)-ray beam. For example, the relative intensities of these six transitions are given by \(3:x:1:1:x:3\), where \(x\) is zero if the \(\gamma\)-ray direction is parallel to the magnetization direction, 4 if the \(\gamma\)-ray direction is normal to the magnetization, and 2 in randomly oriented polycrystalline samples. Thus, for a thin absorber with domain magnetizations in random directions the intensities of lines will be proportional to \(3:2:1:1:2:3\).

**Fig. 3.3.6** The nuclear energy levels in \(^{57}\text{Fe}\) involved in Mössbauer spectroscopy in the case of a pure magnetic interaction. The magnitude of splitting is proportional to the total magnetic field to the nucleus.
3.3.3.4 Combined magnetic and quadrupole interaction

Both the magnetic and quadrupole hyperfine interactions can be simultaneously present, giving expression to an interaction of the nucleus with its environment. However, their effective principal axes are not necessarily co-linear resulting in a more complex behaviour. The formal Hamiltonian is

\[
\hat{H} = -g \mu_B \vec{I} \cdot \vec{B} - \frac{1}{6} e \hat{Q} \cdot \nabla \vec{E}
\]  

(3.3.22)

and it does not have a general analytic solution.

One of the few approximated solutions for a $1/2 \rightarrow 3/2$ transition in $^{57}\text{Fe}$ is the case when the quadrupole interaction is substantially weaker than the magnetic term, and can be treated as a small perturbation of the magnetic interaction. The resultant energy levels are given by

\[
E_{QM} = -g \mu_B B m_z + (-1)^{m_z+1/2} \frac{e^2 q Q}{4} \left( \frac{3 \cos^2 \theta - 1}{2} \right)
\]  

(3.3.23)

where $\theta$ is the angle between the magnetic hyperfine field direction or magnetic axis and the major axis of the electric field gradient tensor. Therefore, all the magnetic hyperfine lines are shifted by a quantity called the quedrupole electric shift and given by:

\[
|\epsilon| = \frac{e^2 q Q}{4} \left( \frac{3 \cos^2 \theta - 1}{2} \right).
\]  

(3.3.24)

The resultant spectra can be observed in Fig 3.3.7.

![Figure 3.3.7](image-url)  

**Fig. 3.3.7** The effect of the quadrupole perturbation on a magnetic hyperfine spectrum for a $3/2 \rightarrow 1/2$ transition.
The angle $\theta$ and the value of $e^2 q Q$ cannot be determined independently from the line position. The line positions are related to the splitting of the energy levels, but not to the relative intensities of these transitions in the recorded spectrum. The intensities arise from the coupling of two angular momentum states, which can be expressed as the product of both an angular dependent term and an angular independent term by

$$A(L, \theta) = C^2(J) \Theta(J, \theta)$$

where $C^2(J)$ is the transition probability of the $\gamma$-ray between two nuclear sublevels, and $\Theta(J, \theta)$ is the angular dependence of the radiation probability at an angle $\theta$ with respect to the quantization axis.

The angular independent term is given by the square of the appropriate Clebsch-Gordan coefficients

$$C^2(J) = \left| \langle I_1 I_2 | m_1 m_2 \rangle \right|^2$$

where the two nuclear spin states $I_1$ and $I_2$ have $I_z$ values of $m_1$ and $m_2$, and their coupling obeys the vector sum $J = I_1 + I_2$ and $m = m_1 + m_2$. $J$ is the multipolarity of the transition, $J = 1$ being bipolar and $J = 2$ being quadrupolar. As the multipolarity of the radiation increases the transition probability decreases.

Most of the Mössbauer transitions take place without a change in parity, so that the radiation is classified as a magnetic dipole (M1) or electric quadrupole (E2) transition. The selection rule for an M1 transition is $\Delta m_z = 0, \pm 1$, and for E2 transition is $\Delta m_z = 0, \pm 1, \pm 2$. In $^{57}$Fe the 14.4 keV transition is primarily dipolar and values for this transition are given in Tab.

The line intensities are related also to the angle between the Mössbauer $\gamma$-ray and the nuclear spin moment. The angular dependent terms, $\Theta(J, \theta)$, are expressed as the radiation probability in a direction at an angle $\theta$ with respect to the quantization axis. The intensity for a polycrystalline sample is obtained by integration over all $\theta$. Coefficients such as in Tab. are necessary in order to interpret the angular dependence of the spectrum. For example, in a magnetic spectrum that have a unique direction of the internal field the outer, middle and inner line expected intensities are related by

$$3:4 \sin^2 \theta:1:1:4 \sin^2 \theta:1:1:4 \sin^2 \theta:3$$

meaning that the outer and inner lines are always in the same proportion but the middle lines can vary in relative intensity between 0 and 4 depending upon the angle between the nuclear spin moments and the $\gamma$-ray. In polycrystalline samples with no applied field there is no angular dependence thus this value averages 2 but in single crystals or under applied fields the relative line intensities can give information about moment orientation and magnetic ordering: transitions have zero intensity when observed along the direction of the field ($\theta = 0^\circ$) and a maximum intensity perpendicular to the field ($\theta = 90^\circ$). The equivalent behavior in the quadrupole spectrum is a 1:3 ratio for the axis.
parallel to the direction of $V_{zz}$ and a 5:3 ratio perpendicular to $V_{zz}$. The magic angle $\theta = 54.7^\circ$ corresponds to a random orientation (the $\gamma$-ray being normal to the ribbon plane).

<table>
<thead>
<tr>
<th>$m_2$</th>
<th>$-m_1$</th>
<th>$m$</th>
<th>$C$</th>
<th>$C^2$</th>
<th>$\Theta$</th>
<th>$\theta = 90^\circ$</th>
<th>$\theta = 0^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\pm \frac{3}{2}$</td>
<td>$\pm \frac{1}{2}$</td>
<td>$+1$</td>
<td></td>
<td>3</td>
<td>$1 + \cos^2 \theta$</td>
<td>3</td>
<td>6</td>
</tr>
<tr>
<td>$\pm \frac{1}{2}$</td>
<td>$\pm \frac{1}{2}$</td>
<td></td>
<td>$\sqrt{\frac{2}{3}}$</td>
<td>2</td>
<td>$2 \sin^2 \theta$</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>$\pm \frac{1}{2}$</td>
<td>$\pm \frac{1}{2}$</td>
<td>$-1$</td>
<td>$\sqrt{\frac{1}{3}}$</td>
<td>1</td>
<td>$1 + \cos^2 \theta$</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>$\pm \frac{3}{2}$</td>
<td>$\pm \frac{1}{2}$</td>
<td></td>
<td></td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\pm \frac{3}{2}$</td>
<td>$-\frac{1}{2}$</td>
<td>$+2$</td>
<td></td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\pm \frac{1}{2}$</td>
<td>$-\frac{1}{2}$</td>
<td>$+1$</td>
<td>$\sqrt{\frac{1}{3}}$</td>
<td>1</td>
<td>$1 + \cos^2 \theta$</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>$\pm \frac{1}{2}$</td>
<td>$-\frac{1}{2}$</td>
<td></td>
<td>$\sqrt{\frac{2}{3}}$</td>
<td>2</td>
<td>$2 \sin^2 \theta$</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>$\pm \frac{3}{2}$</td>
<td>$-\frac{1}{2}$</td>
<td>$-1$</td>
<td>3</td>
<td>$1 + \cos^2 \theta$</td>
<td>3</td>
<td>6</td>
<td></td>
</tr>
</tbody>
</table>

Tab. 3.3.1 Relative probabilities for a dipole $\frac{3}{2} \rightarrow \frac{1}{2}$ transition. $C^2$ and $\Theta$ are the angular independent and dependent terms arbitrarily normalized. Relative intensities for $\theta = 90^\circ$ and $\theta = 0^\circ$ are shown.
CHAPTER 4. EXPERIMENTAL RESULTS

This chapter has the aim to present the experimental results of the samples produced in the laboratory. The first part shows the characteristics of the different ribbons and the production parameters; the second part reports the studies of characterization of the ribbons with XRD, EDS and DSC; the last part shows the results obtained with Mössbauer spectroscopy.

4.1 Production parameters of the ribbons

The objective of this subpart is the presentation of the work conditions and parameters under which the different ribbons were produced in order to explain the differences between their characteristics.

First of all, we prepared the amount of materials that we wanted to obtain of the alloy Fe\textsubscript{71.2-x}C\textsubscript{7.0}Si\textsubscript{3.3}B\textsubscript{5.5}P\textsubscript{8.7}Cr\textsubscript{2.3}Al\textsubscript{2.0}Mo\textsubscript{x}. We chose to study three different composition, substituting Fe for small amounts of Mo in sequence: two series of alloys with \( x = 0, 4.5, 6.5 \) were prepared using pure elements and a powder of Fe\textsubscript{2}P. The total mass of the alloy was 2 grams, so we calculated the ratio for each element using the percentage and the atomic weigh (MA):

\[
\text{Composition Mass} / \text{Moles} = \sum_i (\%_i \cdot MA_i) \tag{4.1.1}
\]

where the index \( i \) is referred to the elements and

\[
\text{Element Moles} = \%_i \cdot \text{Total Moles} = \%_i \cdot \frac{2g}{\sum_i \%_i \cdot MA_i} \tag{4.1.2}
\]

\[
\text{Element Mass} = \text{Element Moles} \cdot MA
\]

obtaining the theoretical mass (g). The balance with which we weight the elements has a precision of \( 10^{-4} \) g, thus the error (at.%) is < 0.1%. The relative atomic error for each element is

\[
\varepsilon = \frac{\text{real at.\%} - \text{at.\%}}{\text{at.\%}} \tag{4.1.3}
\]

and this shows the loss or increase in the real composition relative to the theoretical one.

The Tab. 4.1.1 shows the theoretical composition compared with the real composition of the first three samples that we alloyed in the arc melter.
### L3

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic Weight (g/mol)</th>
<th>Theoretical at.%</th>
<th>Theoretical Mass (g)</th>
<th>Measured at.%</th>
<th>Measured Mass (g)</th>
<th>Relative Atomic Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>26,982</td>
<td>2,0%</td>
<td>0,0232</td>
<td>2,01%</td>
<td>0,0233</td>
<td>0,53%</td>
</tr>
<tr>
<td>Fe</td>
<td>55,845</td>
<td>71,2%</td>
<td>1,2907</td>
<td>71,23%</td>
<td>1,2910</td>
<td>0,04%</td>
</tr>
<tr>
<td>C</td>
<td>12,0107</td>
<td>7,0%</td>
<td>0,0361</td>
<td>6,96%</td>
<td>0,0359</td>
<td>-0,58%</td>
</tr>
<tr>
<td>B</td>
<td>10,811</td>
<td>5,5%</td>
<td>0,0255</td>
<td>5,49%</td>
<td>0,0255</td>
<td>-0,15%</td>
</tr>
<tr>
<td>Si</td>
<td>28,0855</td>
<td>3,3%</td>
<td>0,0398</td>
<td>3,30%</td>
<td>0,0398</td>
<td>-0,02%</td>
</tr>
<tr>
<td>P</td>
<td>30,9738</td>
<td>8,7%</td>
<td>0,0000</td>
<td>8,70%</td>
<td>0,0000</td>
<td>0,04%</td>
</tr>
<tr>
<td>Cr</td>
<td>51,9961</td>
<td>2,3%</td>
<td>0,0514</td>
<td>2,31%</td>
<td>0,0515</td>
<td>0,26%</td>
</tr>
<tr>
<td>Mo</td>
<td>95,94</td>
<td>0,0%</td>
<td>0,0000</td>
<td>0,00%</td>
<td>0,0000</td>
<td>no</td>
</tr>
<tr>
<td>Fe2P</td>
<td>142,6638</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tot</td>
<td>100,00%</td>
<td>2,0000</td>
<td>100,00%</td>
<td>2,0003</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Tab. 4.1.1** Real composition compared with the theoretical one of the three ribbons of the first series: the relative errors are quite small.
Among these elements, only the Fe$_2$P is toxic, so it must be carefully used and avoiding inhalation or contact with the eyes. The melting point of each elements are shown in the Tab. 4.1.2 as well as the melting point of tungsten that is the material used in the arc melter to create the plasma arc. From this table is easily seen how we can melt all the elements without problems.

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>Fe</th>
<th>C</th>
<th>B</th>
<th>Si</th>
<th>P</th>
<th>Cr</th>
<th>Mo</th>
<th>W</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting Point (°C)</td>
<td>660.3</td>
<td>1538</td>
<td>3527</td>
<td>2076</td>
<td>1414</td>
<td>44.2</td>
<td>1907</td>
<td>2623</td>
<td>3422</td>
</tr>
</tbody>
</table>

Tab. 4.1.2 Thermal property of the elements: melting point.

The work conditions for each of the three samples were almost the same:

- All the elements were put together in the copper crucible of the arc melter, with the powder of Fe$_2$P at the top of the other elements;
- The tungsten tip of 2.4mm $\varnothing$ of the arc melter arm was 13 mm long in order to be near the elements;
- The work pressure of Argon in the chamber of the arc melter was about 400 mbar;
- The work current intensity was between 50 and 80A.

We did not achieve the goal of melting homogenously all the elements and thus, create only one ball to put in the quartz crucible of the melt spinner. That was because the plasma arc did not concentrate on the center of the copper crucible, but instead it spread in all the volume. Therefore, the temperature was not high enough to reach the melting point of all the elements. Nevertheless, all the elements got fused together and the homogenization was done with the induction coil of the melt spinner.

Table Tab. 4.1.3 shows the parameters of the wheel and the chamber pressure of the melt spinner used for the production of the three samples. For all the samples we used the quartz tube with the hole of 1mm $\varnothing$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Wheel Speed (m·s$^{-1}$)</th>
<th>Distance tube-wheel (mm)</th>
<th>Chamber Pressure (mbar)</th>
<th>Injection Pressure (mbar)</th>
<th>Thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L3</td>
<td>40</td>
<td>1.15</td>
<td>400</td>
<td>1000</td>
<td>15.7 ± 1.1</td>
</tr>
<tr>
<td>L4</td>
<td>40</td>
<td>1.20</td>
<td>400</td>
<td>1000</td>
<td>29 ± 9</td>
</tr>
<tr>
<td>L5</td>
<td>40</td>
<td>1.20</td>
<td>300</td>
<td>1000</td>
<td>91 ± 18</td>
</tr>
</tbody>
</table>

Tab. 4.1.3 Parameters of the wheel and the chamber pressure of the melt spinner and the ribbons thickness of the first three samples.

We can see from the Tab. 4.1.3 that the thickness of the three ribbons differs among them a lot, even with the work parameters almost equal. This can be a first evidence that a small amount of Molybdenum changes the characteristics of the alloy. In this case a change in the viscosity can be deduced because a
thicker ribbon implies a larger flux of molten alloy colliding with the wheel and a larger flux implies a smaller viscosity. Furthermore, the mechanical characteristics are different: the first one \((x = 0)\) can be bented without cracking and seems to have an elastic behavior, while the last one \((x = 6.5)\) is the most fragile. The one with \(x = 4.5\), has an intermediate behavior. The quality, and consequently the performance of an amorphous ribbon is strongly dependent on the experimental conditions. For example, the quenching rate that governs the amorphicity and the surface roughness are important factors. Other factors that can be mentioned as influential parameters are the thermal conductivity of both the wheel and the molten alloy, the rotating speed, the surface polishing of the wheel, the ejection condition (size and shape of the nozzle, ejection rate, angle, distance) and the viscosity of the molten alloy. Nevertheless, the conditions of quenching prevent a perfect structural and chemical homogeneity of the ribbon [16]. Indeed the quenching rate differ for the dull face (in contact with the rotating wheel) and the shiny face (in contact with the controlled atmosphere). The dull face has a faster quenching rate, and consequently a larger free volume and this causes the presence of local structural and chemical inhomogeneities and thermal stresses in the amorphous material.

For the second series of ribbons we try to change some parameters in order to improve the fusion of metals in the arc melter:

- We chose to melt first the powder of \(\text{Fe}_2\text{P}\) with only B and Al, and only after that add the other elements;
- The tungsten tip of 2.4mm \(\phi\) of the arc melter arm was 6-10 mm long;
- The work pressure of Argon in the chamber of the arc melter was about 500 mbar;
- The work current intensity was between 50 and 80A.

With these changes we obtained a ball with all the elements fused together. Table Tab. 4.1.4 shows the parameters of the wheel and the chamber pressure of the melt spinner used for this second serie of three samples. For all the sample we also used the quartz tube with the hole of 1mm \(\phi\).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Wheel Speed (m·s(^{-1}))</th>
<th>Distance tube-wheel (mm)</th>
<th>Chamber Pressure (mbar)</th>
<th>Injection Pressure (mbar)</th>
<th>Thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L6</td>
<td>40</td>
<td>4.15</td>
<td>400</td>
<td>1000</td>
<td>28 ± 6</td>
</tr>
<tr>
<td>L7</td>
<td>40</td>
<td>1.20</td>
<td>400</td>
<td>700</td>
<td>21 ± 2</td>
</tr>
<tr>
<td>L8</td>
<td>40</td>
<td>1.40</td>
<td>400</td>
<td>800</td>
<td>28 ± 2</td>
</tr>
</tbody>
</table>

**Tab. 4.1.4** Parameters of the wheel and the chamber pressure of the melt spinner and the ribbons thickness of the second three samples.

This time we controlled also the temperature while the metals were melted with a pirometer: all the samples reached a temperature between 1050-1100 °C. There is less difference in the thickness of the three ribbons because we changed the difference in the pressure to compensate the change of viscosity: an increase in the percentage of Mo means a decrease of viscosity, so we compensated it with a decrease of the difference between the chamber and the
deposits pressure, so the fused alloy would go out from the test tube hole with a different force and velocity for each composition.

The mechanical characteristics of the ribbons of this second serie are similar to the ones of the ribbons of the first serie: the sample L6 \((x = 0)\) is wider than the sample L3 and has ragged edges but it can be bended like L3; the sample L7 \((x = 4.5)\) is less fragile than the sample L4 but it is thin and with the ragged edges and its behavior is in the middle between the two other compositions; the last sample L8 \((x = 6.5)\) is narrower than the sample L5 that is thicker and harder, but it is anyway quite fragile and it has holes in the middle and ragged edges.

### 4.2 Results of the x-rays Diffraction (XRD)

We need to know if the ribbon that we made is amorphous or not. In order to obtain this result we studied the ribbons with the x-ray diffraction (XRD) technique. The analysis was made in the European Synchrotron Radiation Facility (ESRF) located in Grenoble, France. The samples were analyzed in the baemline BM16 that works in an energy range between 6.5 - 17 keV (1.90 - 0.73 Å) and the ray focal spot is 200 x 400 microns. BM16 is rapidly and easily tunable and has an optical configuration specifically designed to facilitate anomalous diffraction experiments. The available energy range covers most commonly used K and L edges.

The experimental hutch at BM16 contains both a PX (Protein Crystallography) station and a Non Crystalline Diffraction (NCD) station; for the XRD experiment the PX station is used. The detector used is the Quantum 315r that has a screen where the rings can be observed.

In the **Fig. 4.2.1** we can see the diffraction pattern of the first series of ribbons.

![Fig. 4.2.1](image)  
**(a)** XRD spectrum in a diffractogram of the first series of ribbons;  
**(b)** Diffraction rings on a flat plane detector of the sample L3.
It can be observed from the three spectra of Fig. 4.2.1 (a) that there are not narrow peaks that suggest the existence of a crystalline phase. It is worth to note the presence of a broad band around of \( q \approx 32 \) that indicates the mean interatomic distance in the amorphous material. The three curves seem to have the same broad peak meaning that all the ribbons are amorphous. In the Fig. 4.2.1 (b) it is possible to see an example of the diffraction rings obtained with the sample L3.

The analysis is repeated for the second series of ribbons and the resultant spectra are shown in Fig. 4.2.2 (a).

Also for these three ribbons there are not sharp peaks that suggest the existence of a crystalline phase. The broad band is always around \( q \approx 32 \). Therefore, the ribbons are also amorphous. In the Fig. 4.2.2 (b) the diffraction rings produced by the sample L7 are shown.

4.3 Results of the EDS analysis

The method used to determine the real chemical composition of the ribbons and to check how much differ from the theoretical one is the EDS (Energy Dispersive Spectroscopy) of x-rays made in a SEM. The results of this study are not very precise because the equipment can only detect the elements that have an atomic weight greater than the one of the Aluminium. Thus, in our composition we could not see the right percentage of Boron and Carbon, only the percentages of Aluminium, Silicon, Phosphorus, Chromium and Iron. Another problem was that the detector could only do a qualitative measure of Molybdenum, that is it only detects if there is Mo or not, but without a quantitative measure.
**Fig. 4.3.1** Electron microscopy Jeol JSM-840 utilized to analyzed the first series of ribbons.

We analyzed the samples in three different points in each ribbon and on both sides; then we did an average between the measured weight percentage of the elements in the points chosen and at the end transformed it to atomic percentage.

Table **Tab. 4.3.1** on the left reports the average of the weight and atomic percentage of each detected element in some of the analyzed points for the first series of ribbons. From the table it seems that the analysis can also detect the elements C and Al, but the measures are not reliable because the C is present also in the ribbon support for the SEM and because the two elements have a too small atomic number to be detected with precision.

Basically, it is necessary to subtract from the total weight the sum of the three unreliable elements, and secondly to calculate the percentage that it represents relative to the total. The applied formula to calculate the total percentage composed only by the detected elements is

\[
\% \text{Useful Sample} = \frac{\text{Total} - (\% C + \% Al + \% B)}{\text{Total}} \cdot 100
\]  

(4.3.1)

The next step is to normalize the other components simply dividing the weight percentage of every element for the useful sample percentage that are the data that we can observe in the **Tab. 3.3.1** on the right. The sum of the percentages has to be the same as the one at the beginning to asses the validity of the data treatment.

Finally, to obtain the atomic percentage of every element it is necessary to consider the atomic mass of each element dividing the weight percentage for the atomic mass and normalizing it with the following expression for each element:

\[
\text{at} \%. = \frac{\text{element weight} \%}{\text{element MA}} \cdot \frac{\sum_{i=1}^{n} \text{element weight} \%}{\sum_{i=1}^{n} \text{element MA}} \cdot 100
\]  

(3.3.2)
where the atomic weights are the ones shown in table Tab.4.1.1. The results are reported in table Tab. 4.3.1 in the last column.

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight%</th>
<th>Atomic%</th>
<th>Element</th>
<th>Normal.W%</th>
<th>Atomic%</th>
</tr>
</thead>
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<td>21.705</td>
<td>B K</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C K</td>
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<td>17.295</td>
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<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Al K</td>
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<td>0.43</td>
<td>Al K</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Si K</td>
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<td>1.99</td>
<td>Si K</td>
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<td>P K</td>
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<td>4.995</td>
<td>P K</td>
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<td>8.2489</td>
</tr>
<tr>
<td>Cr K</td>
<td>2.91</td>
<td>1.835</td>
<td>Cr K</td>
<td>3.3236</td>
<td>3.0263</td>
</tr>
<tr>
<td>Fe K</td>
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<td>51.75</td>
<td>Fe K</td>
<td>100.7824</td>
<td>85.4420</td>
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<tr>
<td>Totals</td>
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<td>100</td>
<td>Totals</td>
<td>111.45</td>
<td>100</td>
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<th>Element</th>
<th>Normal.W%</th>
<th>Atomic%</th>
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</tr>
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<td>C K</td>
<td>3.449</td>
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<td>-</td>
</tr>
<tr>
<td>Al K</td>
<td>1.295</td>
<td>2.131</td>
<td>Al K</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Si K</td>
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<td>Si K</td>
<td>2.5780</td>
<td>4.8361</td>
</tr>
<tr>
<td>P K</td>
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<td>4.474</td>
<td>P K</td>
<td>3.3240</td>
<td>5.6541</td>
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<tr>
<td>Cr K</td>
<td>0.577</td>
<td>0.494</td>
<td>Cr K</td>
<td>0.6149</td>
<td>0.6231</td>
</tr>
<tr>
<td>Fe K</td>
<td>88.405</td>
<td>70.334</td>
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<td>94.2160</td>
<td>88.8867</td>
</tr>
<tr>
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<td>-</td>
<td>-</td>
<td></td>
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<td>Si+P+Cr+Fe</td>
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<table>
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<th>Weight%</th>
<th>Atomic%</th>
<th>Element</th>
<th>Normal.W%</th>
<th>Atomic%</th>
</tr>
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<td>4.85</td>
<td>B K</td>
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<td>-</td>
</tr>
<tr>
<td>C K</td>
<td>2.034</td>
<td>7.996</td>
<td>C K</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Al K</td>
<td>0.883</td>
<td>1.551</td>
<td>Al K</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Si K</td>
<td>1.966</td>
<td>3.306</td>
<td>Si K</td>
<td>2.0496</td>
<td>3.8638</td>
</tr>
<tr>
<td>P K</td>
<td>5.188</td>
<td>7.911</td>
<td>P K</td>
<td>5.4085</td>
<td>9.2452</td>
</tr>
<tr>
<td>Cr K</td>
<td>3.546</td>
<td>3.225</td>
<td>Cr K</td>
<td>3.6967</td>
<td>3.7642</td>
</tr>
<tr>
<td>Fe K</td>
<td>84.104</td>
<td>71.161</td>
<td>Fe K</td>
<td>87.6783</td>
<td>83.1268</td>
</tr>
<tr>
<td>Mo</td>
<td>-</td>
<td>-</td>
<td></td>
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<tr>
<td>Totals</td>
<td>98.833</td>
<td>100</td>
<td>Totals</td>
<td>98.833</td>
<td>100</td>
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<tr>
<td>Si+P+Cr+Fe</td>
<td>95.923</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Tab. 4.3.1 The tables on the left represent the average between 6 analyzed points of the weight and atomic percentage measured with the SEM, while on the right hand the table shows normalized percentages of the first series of ribbons.
The last part of the study of these data is to compare the atomic percentage of the normalized component with the theoretical normalized percentage, excluding the four elements and normalizing the other components respect to the total as if the samples were composed only by the four detected elements:

\[
\% \text{ Element} = \frac{\% \text{ th. Element}}{\% \text{ Total (Si, P, Cr, Fe)}} \cdot 100
\] (4.3.3)

The results can be observed in table Tab 4.3.2.

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>P</th>
<th>Cr</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>L3 exp.</td>
<td>3.2827</td>
<td>8.2489</td>
<td>3.0263</td>
<td>85.4420</td>
</tr>
<tr>
<td>L3 th.</td>
<td>3.8596</td>
<td>10.1754</td>
<td>2.8901</td>
<td>83.2749</td>
</tr>
<tr>
<td>L4 exp.</td>
<td>4.8361</td>
<td>5.6541</td>
<td>0.8231</td>
<td>88.8867</td>
</tr>
<tr>
<td>L4 th.</td>
<td>4.0741</td>
<td>10.7407</td>
<td>2.8395</td>
<td>82.3457</td>
</tr>
<tr>
<td>L5 exp.</td>
<td>3.8638</td>
<td>9.2452</td>
<td>3.7642</td>
<td>83.1268</td>
</tr>
<tr>
<td>L5 th.</td>
<td>4.1772</td>
<td>11.0127</td>
<td>2.9114</td>
<td>81.8987</td>
</tr>
</tbody>
</table>

Tab. 4.3.2 Normalization of the components detected with EDS analysis of the ribbons of the first series compared with the theoretical normalized percentage.

From the table we can observe that samples L3 and L5 have a composition quite similar to the theoretical one, while the sample L4 is very different. An explanation for this elements loss is the possibility that part of the powder of $\text{Fe}_2\text{P}$ went out from the hole of the quartz crucible, and because part of the molten liquid got attached to the crucible and did not get injected to the wheel. The first and the third ribbon, even if something did not melt, seems to be more similar to the theoretical composition and it could mean that in the arc melter and successively in the melt spinner the elements melted quite homogenously.

In the Fig. 4.3.1 an example of an EDS spectrum of the sample L3 shows the peaks corresponding to the different elements while Fig. 4.3.2 shows an image of the ribbon surface of the sample L3 by means of the detector of secondary electrons (SE).

**Fig. 4.3.1** EDS spectrum of the sample L3.
Fig. 4.3.2 *Three images SE of the sample L3 at different magnitude.*

We also analyzed the second serie of ribbons with the EDS of a SEM. We studied the ribbons in the same way of the other serie: we choose some points on either side of the ribbon, and then we did the average for each of the measured elements in weight percentage transforming it also into atomic percentage, as it is shown in the Tab. 4.3.3 at the left. At the end, the data were normalized relative to the composition formed only by Si, P, Cr and Fe, as it is shown in table Tab. 4.3.3 on the right.

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight%</th>
<th>Atomic%</th>
<th>Element</th>
<th>Normal.W%</th>
<th>Atomic%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C K</td>
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<td>15.217044</td>
<td>C K</td>
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<td>-</td>
</tr>
<tr>
<td>Al K</td>
<td>0.536</td>
<td>0.9131516</td>
<td>Al K</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Si K</td>
<td>1.96</td>
<td>3.2079394</td>
<td>Si K</td>
<td>2.0523</td>
<td>3.8249</td>
</tr>
<tr>
<td>P K</td>
<td>4.966</td>
<td>7.3699578</td>
<td>P K</td>
<td>5.0000</td>
<td>8.7874</td>
</tr>
<tr>
<td>Cr K</td>
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<td>4.435403</td>
<td>Cr K</td>
<td>2.8942</td>
<td>2.9135</td>
</tr>
<tr>
<td>Fe K</td>
<td>86.072</td>
<td>70.848367</td>
<td>Fe K</td>
<td>90.1274</td>
<td>84.4742</td>
</tr>
<tr>
<td>Totals</td>
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<td>100</td>
<td>Totals</td>
<td>100.274</td>
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</tr>
<tr>
<td>Si+P+Cr+Fe</td>
<td>95,500</td>
<td></td>
<td>Si+P+Cr+Fe</td>
<td>94,500</td>
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</tr>
</tbody>
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<table>
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<tr>
<th>Element</th>
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<th>Normal.W%</th>
<th>Atomic%</th>
</tr>
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<tr>
<td>C K</td>
<td>4.9733</td>
<td>18.44399</td>
<td>C K</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Al K</td>
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<td>0.8584356</td>
<td>Al K</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Si K</td>
<td>2.0467</td>
<td>3.2460153</td>
<td>Si K</td>
<td>2.1657</td>
<td>4.0224</td>
</tr>
<tr>
<td>P K</td>
<td>5.54</td>
<td>7.9669912</td>
<td>P K</td>
<td>5.8620</td>
<td>9.8727</td>
</tr>
<tr>
<td>Cr K</td>
<td>2.7267</td>
<td>2.3358509</td>
<td>Cr K</td>
<td>2.8852</td>
<td>2.8946</td>
</tr>
<tr>
<td>Fe K</td>
<td>84.1867</td>
<td>67.148717</td>
<td>Fe K</td>
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<td>83.2103</td>
</tr>
<tr>
<td>Totals</td>
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<td>100</td>
<td>Totals</td>
<td>99.9934</td>
<td>100</td>
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<tr>
<td>Si+P+Cr+Fe</td>
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<td></td>
<td>Si+P+Cr+Fe</td>
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Experimental results

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<th>Element</th>
<th>Weight%</th>
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<th>Element</th>
<th>Normal.W%</th>
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<td>-</td>
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<td>Si K</td>
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<td>Si K</td>
<td>2.5546</td>
<td>4.3830</td>
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<tr>
<td>P K</td>
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<td>P K</td>
<td>6.9442</td>
<td>10.8033</td>
</tr>
<tr>
<td>Cr K</td>
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</tr>
<tr>
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<td>Totals</td>
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</tbody>
</table>

Tab. 4.3.3 (Begins in the previous page) The tables on the left represent the average between 6 analyzed points of the weight and atomic percentage measured with the SEM, while on the right hand the table shown normalized percentage of the second serie of ribbons.

Now we need to compare with the theoretical percentage. The results can be observed in table Tab. 4.3.4.

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<th>P</th>
<th>Cr</th>
<th>Fe</th>
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</thead>
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<td>84.4742</td>
</tr>
<tr>
<td>L6 th.</td>
<td>3.8596</td>
<td>10.1754</td>
<td>2.6901</td>
<td>83.2749</td>
</tr>
<tr>
<td>L7 exp.</td>
<td>4.0224</td>
<td>9.8727</td>
<td>2.8946</td>
<td>83.2103</td>
</tr>
<tr>
<td>L7 th.</td>
<td>4.0741</td>
<td>10.7407</td>
<td>2.8395</td>
<td>82.3457</td>
</tr>
<tr>
<td>L8 exp.</td>
<td>4.3830</td>
<td>10.8033</td>
<td>2.9179</td>
<td>81.8959</td>
</tr>
<tr>
<td>L8 th.</td>
<td>4.1772</td>
<td>11.0127</td>
<td>2.9114</td>
<td>81.8987</td>
</tr>
</tbody>
</table>

Tab. 4.3.4 Normalization of the components detected with EDS analysis of the ribbons of the second serie compared with the theoretical normalized percentage.

This time, all the experimental compositions are quite similar to the theoretical percentage. This means that the attempted solution in the sample preparation improved the quality of the ribbons.

Figure Fig. 4.3.3 (a) is an example of an EDS spectrum of the sample L6 that shows the peaks corresponding to the different elements while Fig. 4.3.3 (b) is an image of the ribbon surface of the sample L6 by means of the detector of secondary electrons (SE).
4.4 Mössbauer spectroscopy Analysis

In this section we study the possible changes in the local structure of the produced ribbons as the concentration of Mo and Fe is modified. To perform this analysis, transmission Mössbauer spectroscopy (TMS) was carried out at room temperature on the amorphous sample, before and after the annealing treatments, using a 25 mCi source of $^{57}$Co in a Rh matrix. The isomer shift values are given relative to room temperature $\alpha$-Fe (IS = -0.1 mm/s). The spectra were fitted with Brand’s NORMOS program [17]. The amorphous structure has been fitted by superimposing subspectra from 0.0 T to 35.0 T with steps of 1.0 T, giving rise to a distribution of hyperfine magnetic fields. A linear correlation between the isomer shift and the hyperfine magnetic fields has been also included.

4.4.1 As-quenched samples

The magnetic behavior of the amorphous Fe$_{71.2-x}$C$_{7.0}$Si$_{3.3}$P$_{8.7}$Cr$_{2.3}$Al$_{2.0}$Mo$_x$ alloy can be investigated by the Mössbauer effect. The several types of environments in which the Fe atoms can reside can be derived from the hyperfine parameters, which are the isomer shift (IS), the quadrupole splitting (QS) and the mean value of the hyperfine field as well as the shape of its distribution. All these parameter readily available from the Mössbauer fitting. All these parameters are related to the local atomic environment [18].

This section reports the Mössbauer spectra of the as quenched ribbons. The experimental hyperfine distribution, that in the case of amorphous samples is the most relevant parameter, can be interpreted in terms of local environments [16].

Experimental TMS spectra of the first serie of samples are shown in Fig. 4.4.1. The dots represents the experimental points and the solid lines the corresponding fit. The spectra consist of broadened lines characteristic of the amorphous system and were fitted, as stated before, using an unique hyperfine field distribution (0 - 35 T) shown in Fig. 4.4.2.
The spectrum of L3 is a typical Mössbauer spectrum of an Fe-based metallic glass in a ferromagnetic phase. It is characterized by a unique sextet with broad lines, which corresponds to a ferromagnetic disordered alloy. The lines are characterized by high values of the full width at half maximum, a typical feature of structurally disordered materials [19]. Such spectra are observed in amorphous magnetic solids in which there is a large number of non-equivalent Fe sites. The fact that each of the six spectral lines show no fine structure suggest that the hyperfine field is quasi-continuous [20]. The asymmetrical shape that can occur is due to the correlation between the isomer shift and the magnetic hyperfine field. This is consistent with the randomness of the atomic arrangements [21].

In L4, the Mössbauer spectrum does not present any significant change with respect the ribbon without Mo because the six ferromagnetic peaks are still present. Nevertheless, as will be shown later, the hyperfine magnetic field distribution presents interesting changes.

The spectrum of L5 is quite different showing the presence of a well resolved doublet. It can be seen that the traces of magnetically split components are disappearing, which is a different feature from the observed in the other amorphous alloys. The broadened doublet-like structure indicates a
paramagnetic behavior and a fully amorphous structure [22]. Thus, the local structure is changing with the addition of Mo.

Mössbauer spectroscopy allows a direct measurement of the effective or internal magnetic field at the nucleus, through the so-called hyperfine field \( B \). In addition, the intensities of intermediate lines describe the orientation of the mean magnetization direction of \( B_f \) according to the \( \gamma \)-beam direction (see section 3 in chapter 3).

The average hyperfine field of the distribution of \( L_3 \) is \( <B> = 20.1 \pm 0.1 \) T, a typical value for a ferromagnetic disordered phase. For \( x = 4.5 \), the shape of the hyperfine field distribution is essentially the same as for \( x = 0 \) with a well defined maximum at high values of the hyperfine field and a satellite at the low-B tail of the distribution. The maximum is moving towards smaller values of the hyperfine field because there are less Fe atoms and the average distance between them is bigger. In fact, Mo atoms have an atomic radius slightly bigger Fe atoms and both have a bcc structure at room temperature; thus, the substitution of Mo atoms leads to an anisotropic change in the unit cell of the Fe structure, assuming a random distribution of Mo over the Fe sites [19]. For \( x = 6.5 \), the values of the hyperfine field are closer to those of a paramagnetic material and the shape of the distribution changed: the maximum present in the other two distribution disappears while the satellite at low B increases. This could means that the quantity of Mo is high enough to change the properties of the alloy and reduce its magnetic interaction. Moreover, from the shape of the hyperfine field distribution, the reduction of B can not be attributed only to a further substitution of Fe by Mo, but to the destruction of the ferromagnetic local structure.

Both Fig. 4.4.1 and Fig. 4.4.2 show that small additions of Mo lead to substantial changes in the spectra: the substitution of a small content of Mo atoms for Fe leads to significant changes in the Mössbauer spectrum, consisting in a broadening of the absorption lines and a decrease of the overall magnetic hyperfine interaction.
In table Tab. 4.4.1 the values of the Mössbauer spectroscopy parameters of the ribbons are shown.

<table>
<thead>
<tr>
<th></th>
<th>L3</th>
<th>L4</th>
<th>L5</th>
</tr>
</thead>
<tbody>
<tr>
<td>BHF (T)</td>
<td>20.1 (1)</td>
<td>16.6 (1)</td>
<td>12.6 (1)</td>
</tr>
<tr>
<td>δ (mm/s)</td>
<td>0.14 (9)</td>
<td>0.13 (2)</td>
<td>0.13 (1)</td>
</tr>
<tr>
<td>∆ (mm/s)</td>
<td>-0.02 (1)</td>
<td>0.03 (1)</td>
<td>-0.00 (1)</td>
</tr>
<tr>
<td>I2/I3</td>
<td>2.85 (8)</td>
<td>2.6 (1)</td>
<td>2.7</td>
</tr>
</tbody>
</table>

Tab. 4.4.1 Hyperfine parameters of the ribbons L3, L4 and L5: BHF is the average hyperfine field; δ is the isomer shift relative to α-Fe; ∆ is the quadrupole splitting; I2/I3 is the ratio between the second and the third lines of the spectrum.

Table Tab. 4.4.1 shows that the hyperfine field decreases as expected because in the material there are less iron atoms. The isomer shift δ and the quadrupole splitting ∆ are independent of the amount of Mo and have values typical of amorphous phases.

In Fig. 4.4.3 and Fig. 4.4.4 the Mössbauer spectra and the hyperfine field distribution of the second serie of ribbons are shown to compare them with the previous ones.

Fig. 4.4.3 Experimental Mössbauer spectra (dots) with the corresponding fitting (solid line) of the second serie of as-quenched ribbons.
The three Mössbauer spectra are quite similar to the ones of the first serie with the same tendency to loss the ferromagnetic properties with the addition of Mo that leads to a typical paramagnetic spectrum.

![Fig. 4.4.4 Hyperfine field distribution for the second series of the three as-quenched ribbons with different Mo content.](image)

Even in this case, the trend of the hyperfine fields are the same as in the previous ribbons: the hyperfine magnetic field distribution of the ribbon L6 has its maximum around 23 T, and it decreases to lower values of B with the addition of Mo, while the satellite on the left increases and shifts the mean hyperfine field value to 12 T.

In table **Tab. 4.4.2** there are the values of the parameters of the ribbons calculated from the fitting.

<table>
<thead>
<tr>
<th></th>
<th>L6</th>
<th>L7</th>
<th>L8</th>
</tr>
</thead>
<tbody>
<tr>
<td>BHF (T)</td>
<td>20.68 (4)</td>
<td>15.12 (7)</td>
<td>12.94 (5)</td>
</tr>
<tr>
<td>δ (mm/s)</td>
<td>0.16 (9)</td>
<td>0.13 (1)</td>
<td>0.15 (2)</td>
</tr>
<tr>
<td>Δ (mm/s)</td>
<td>-0.04 (1)</td>
<td>0.02 (1)</td>
<td>-0.02 (1)</td>
</tr>
<tr>
<td>I₂/I₃</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>

**Tab. 4.4.2** *Hyperfine parameters of the ribbons L6, L7 and L8: BHF is the average hyperfine field; δ is the isomer shift relative to α-Fe; Δ is the quadrupole splitting; I₂/I₃ is the ratio between the second and the third lines of the spectrum that is fixed.*

Similarly, the hyperfine field decreases while the other parameters remain more or less constant. This confirms that the previous results obtained with the
Experimental results

analysis of the first serie of ribbons (that as previously seen do not have the theoretical composition) are equally significative of the behavior of these Fe-base amorphous alloys.

4.4.2 Estimation of the reduction of the hyperfine magnetic field

From the distribution of the hyperfine magnetic field obtained with Mössbauer spectroscopy it is possible to observe that the average field diminishes. Therefore, we can try to estimate the reduction caused by the substitution of Fe by Mo atoms and to check if this substitution is enough to explain the observed reduction.

Mo is soluble in α-Fe lattice up to ~2 at. % assuming a random distribution of Mo atoms in a bcc lattice. For example, the concentration of 2 at. % implies that 85% of Fe atoms would have 8 Fe atoms as near neighbours (NN), 14% would have 7 Fe and 1 Mo as NN and 1% would have 6 Fe and 2 Mo as NN [23]. We assumed that the substitution of Fe atoms by Mo atoms reduces the magnetic field linearly. Therefore, Mo atoms are assumed to be distributed randomly in a bcc-lattice (that is a first approximation due to the fact that Fe atoms are in an amorphous matrix and not in crystalline lattice). The perfectly random disorder in a solid solution composed by two elements $A_x B_{1-x}$ can be described by means of binomial distribution [21]. The probability for an iron atom to be surrounded by $k$ Fe atoms (from 0 to 8) is thus given by:

$$P_{n=8}(c,k) = \binom{n}{k} c^k (1-c)^{n-k} = \frac{n!}{k!(n-k)!} c^k (1-c)^{n-k}$$

where $n$ is the number of NN (in the present case equal to 8), $c$ is the Fe content (in %), and $k = 0, ..., 8$. This probability can be seen in figure Fig. 4.4.5. For systems containing more than two kinds of atoms the number of parameters becomes extremely high.

![Fig. 4.4.5](image)

*Fig. 4.4.5 The probability for an iron atom to have $k$ Fe atoms as nearest neighbors in a bcc structure.*
The value of the magnetic field $B_{\text{max}}$ for $n = 8$ is set such that the average field obtained from the binomial distribution coincides with that measured for $x = 0$ (L3):

$$
\bar{B}_{\text{TMS}} = \bar{B}_{\text{binom}}
$$

$$
\bar{B}_{\text{binom}} = \frac{1}{\sum_i P_i} \sum_i P_i B_i
$$

where $P_i$ is the probability of the binomial distribution and $B_i$ are the hyperfine field calculated in a linear approximation: $B_i = (B_{\text{max}} / 8) \cdot n_i$.

In figure **Fig. 4.4.7** we can see that the line calculated with the binomiaal distribution does not reproduce well the real trend of the hyperfine magnetic field derived from the Mössbauer spectroscopy. Therefore, the replacement of Fe by Mo can not explain the observed reduction of $B$. This can mean that Mo atoms act not only as substitutional atoms, but also induce local structural changes in the glass.

**Fig. 4.4.7** The trend of the average magnetic hyperfine field as a function of the Mo content calculated with the Mössbauer spectroscopy (TMS) and with the binomial approximation for the first serie of ribbons.

The same model can be applied to the other three samples. The result is reported in **Fig. 4.4.8**.
Fig. 4.5.1 The trend of the average magnetic hyperfine field as a function of the Mo content calculated with the Mössbauer spectroscopy (TMS) and with the binomial approximation for the second serie of ribbons.

Even in this case, the result is the same as the previous one: the average hyperfine field decreases more rapidly than the field calculated with the binomial distribution.

4.5 Thermal Analysis

The next step is to perform a proper thermal treatments to the ribbons in order to induce their structural relaxation. In general, annealing treatments under controlled atmosphere can be applied to as-quenched MGs in order to stabilize the magnetic properties, to reduce the thermal stresses, to remove local homogeneities and to control induced magnetic anisotropy. For this reason, differential scanning calorimetry (DSC) was made to the as quenched ribbons and used to design the proper heat treatments to induce relaxation in the glasses. The efficiency of thermal treatments may be easily checked by Mössbauer experiments.

4.5.1 DSC analysis

In this DSC curves the exothermic reactions are shown with a negative peak. The DSC curves for the produced metallic glasses are presented in Fig. 4.5.1. It is found that the DSC curve shows a double exothermic peak, indicating a two-step crystallization process. The first and the second crystallization temperatures, $T_{x1}$ and $T_{x2}$, are defined at the onset temperatures of the first and second peaks, respectively, and are given in the figure. The glass transition temperature $T_g$ defined by the temperature at which the exothermic curve bends upwards is also given.
**Fig. 4.5.1** At the left, DSC heating curves of the second series of amorphous ribbons; at the right, the table shows the value of the glass transition temperature ($T_g$), the onset temperature of the first crystallization event ($T_{x1}$) and the supercooled liquid region ($\Delta T_x = T_{x1} - T_g$).

From these results it is possible to see that with the substitutions of Mo for Fe the glass transition temperature ($T_g$) and the onset temperature of the first crystallization event ($T_{x1}$) increases, indicating that the amorphous phase can be stabilized at higher temperatures [1]. The extent of the supercooled liquid regions ($\Delta T_x = T_{x1} - T_g$) is often regarded as a parameter to assess the GFA of an alloy. Here, the alloys containing Mo present wider supercooled liquid regions than the alloy without Mo, thus it can be stated that the partial substitution of Mo for Fe improves the GFA.

### 4.5.2 Heat treatment

After the DSC analysis, we chose the temperatures suitable for the heat treatments. Two different heat treatments were applied to the ribbons: the first treatment was made at 80ºC below $T_g$ and 100ºC below $T_{x1}$ whereas the second treatment was made around $T_g$ and 30ºC below $T_{x1}$. Both heat treatments were made in a furnace at 10 K/min up to:

<table>
<thead>
<tr>
<th></th>
<th>$T_g$ (ºC)</th>
<th>$T_{x1}$ (ºC)</th>
<th>$\Delta T_x$ (ºC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L6</td>
<td>480</td>
<td>500</td>
<td>20</td>
</tr>
<tr>
<td>L7</td>
<td>490</td>
<td>525</td>
<td>35</td>
</tr>
<tr>
<td>L8</td>
<td>495</td>
<td>535</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>HT-I</td>
<td>HT- II</td>
<td></td>
</tr>
<tr>
<td>-----</td>
<td>--------</td>
<td>--------</td>
<td></td>
</tr>
<tr>
<td>L3</td>
<td>403 °C</td>
<td>478 °C</td>
<td></td>
</tr>
<tr>
<td>L4</td>
<td>422 °C</td>
<td>497 °C</td>
<td></td>
</tr>
<tr>
<td>L5</td>
<td>429 °C</td>
<td>504 °C</td>
<td></td>
</tr>
</tbody>
</table>

Both treatments reach at a temperature below $T_{x1}$, where the first exothermic event begins, thus, the ribbons remain amorphous but indifferent degrees of structural relaxation of the as-quenched glassy state. Mössbauer spectroscopy was used to check the effects of these heat treatments in the local environment of the Fe atoms.
Fig. 4.5.2 Mössbauer spectroscopy and hyperfine field distribution of the ribbons L3, L4, L5 after the two heat treatments compared with those of the three as-quenched ribbons.

The left part of Fig. 4.5.2 shows the three Mössbauer spectra (as quenched, after the first heat treatment HT-I and after the second HT-II) of the three ribbons L3, L4 and L5. The spectra after the two heat treatments do not present great changes, but looking at the hyperfine field distribution on the right part of
the Fig. 4.5.2 it is possible to see that the heat treatments induce changes in the ribbons L3 and L5 but not in L4 (x = 4,5 at.%) that coincides with the composition with highest GFA. Thus, the most stable composition corresponds to the alloy with the highest GFA.
CHAPTER 5. CONCLUSIONS

In the course of this work, the production of metallic glass alloys has been analyzed in order to improve the production conditions with the arc melter, to obtain more homogeneous ribbons with the melt spinner and thus, assure the reproducibility of the final material. The aim was to obtain more control over the preparation of the MGs samples to be sure that the ribbons have a composition as close as possible to the theoretical one.

With respect the arc melter, the optimal conditions require the use of a tungsten tip 13 mm long in order to be close enough to the elements to melt and the use of the copper crucible with the smaller hole to better focalize the plasma beam. Moreover, it has been concluded that is better to prepare the alloy in a two steps process: firstly to melt the elements that are in powder with some of the bulk ones and secondly, melt the resulting ball with the restan elements. The main factor that controls the ribbon production in the melt spinner has been the pressure difference between the chamber and the injection pressure. As teh different alloys produced have different viscosity, the use of the same pressure difference results in ribbons with different thickness and hence, difficult to compare between them. Moreover, this difference is also important in order to be sure to inject all the molten material into the copper wheel. XRD analysis confirmed the amorphicity of all the produced ribbons.. Because the choosen alloy has a great percentage of Fe, we could analyze the ribbons with the Mössbauer spectroscopy technique to see if the changes of the hyperfine parameters can be related with the change in the GFA of the amorpous alloy.

The high Fe content of the studied alloys is the responsible of the shape of the TMS spectra for $x = 0$ and 4.5. These spectra correspond to a ferromagnetic disordered phase and are similar to those obtained for other compositions [24,25]. As Mo has an atomic radius similar to the Fe, in small amounts it acts as a substitutional atom replacing the Fe in the disordered structure. Thus, Fe nuclei have in average less Fe neighbour atoms with the consequent diminution of the average hyperfine field. Although the shape of the hyperfine field distribution is similar for the two cases, it can be observed how the relative percentage of environments with a low B value (around 10 T) increases, indicating that the Mo atoms can produce changes in the local structure. These changes are more evident in the alloy with $x = 6.5$, in which case the amount of paramagnetic and ferromagnetic environments is similar. The resulting TMS spectra lost the characteristic six line pattern of the ferromagnetic structures. A further reduction of B is obtained, but from the shape of the hyperfine field distribution, this reduction can not be attributed to a further substitution of Fe by Mo, but to the destruction of the ferromagnetic local structure.

In fact, assuming the local structure of the metal glasses to be a bcc structure with Mo atoms distributed randomly and calculating the probability of first neighbours with a binomial distribution, it is possible to see that the TMS hyperfine field decreases more rapidly than the calculated one. This is a confirmation that Mo atoms change the local structure of the material and not only substitute the Fe atoms.

Also a calorimetric study was made in order to choose the most suitable heat treatments to to induce relaxation in the glasses. Two different heat treatments
were applied to the ribbons, the first at 80ºC below \( T_g \), and the second around \( T_g \). Then the relaxed ribbons were studied with the Mössbauer spectroscopy technique and it has been found that only in the ribbon with \( x = 4.5 \) the hyperfine field distribution do not change.

Taking into account the fact that the highest GFA for these alloys was attained for \( x = 4.5 \) and that the local structure determined by TMS is different, it can be concluded that the local configuration of the atoms in an alloy play an important role in determining its GFA. In the present case, the GFA seems favoured by a structure that, although disordered, is between a local ferromagnetic order and a local paramagnetic order. That lack of homogenity in the structure prevents the nucleation. And that fact is also the responsible of the thermal stability of this particular composition.

In conclusion, in this work Mössbauer spectroscopy was used to obtain information about the local structure of Fe-based MGs and to relate that information to its GFA.

Based on the research made in this thesis, further work will include the study of the effect of Mo substitution in the local structure by means of EXAFS. The obtained information combined with the results of Mössbauer spectroscopy will allow to deduce the changes in the number of neighbours and in the interatomic distances.

Also the relation between atomic contents of metal (Fe,Mo,Al,Cr) and non-metal (P,C,S,B) elements can change the properties of the metallic glass, and it is interesting to study for example the changes with the Cr-doping concentration always with EXAFS and related with Mössbauer spectroscopy.

The EXAFS spectra, together with diffraction data and Mössbauer spectra, will be employed for simulation of the MG structure using reverse Montecarlo method. This will allow to determine the structure of the amorphous steel and the preferential localization of the doping atoms, because Fe atoms can have two main kinds of environments, either with or without Mo neighbours, due to the different behaviour of substitutional non-metal (P,Si) and interstitial non-metal (C,B) in a dense packed local structure. One could imagine that those environments are topologically different in some way, and that there could be alternate packing of both Mo-neighbour and Mo-free environments.

This may increase the GFA because of the competition of both topological options (confusion principle), but the objective is how to check this theory and find out if there are and which are the other components that may increase the GFA. For this purpose, it is possible to study simpler compositions, maybe with less elements, to try to understand the role of each component in the GFA.
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APPENDIX

Title: Production and Characterization of Fe-based metallic glasses

Author: Laura Serena Facchini

Director: Daniel Crespo Artiga

Data: 20 juny 2008
A.1 X-Rays Diffraction (XRD)

The x-ray diffraction (XRD) technique is a non-destructive analytical technique useful to obtain information about crystallographic structure for phase identification in a material. The ability of x-rays to penetrate matter differentially, as a function of density and elemental composition, was recognized almost immediately after their discovery and led to widespread applications for observing the internal structure of the materials.

Max von Laue, in 1912, discovered that crystalline substances act as three-dimensional diffraction gratings for X-ray wavelengths similar to the spacing of planes in a crystal lattice allowing the study of crystal structures and atomic spacing.

X-ray diffraction is based on the constructive interference of monochromatic x-rays in a crystalline sample. These x-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample. This technique is based on the observation of the scattered intensity of the x-ray beam from the sample as a function of the incident angle and the polarization, and wavelength of the X-rays. The atomic planes of the crystal cause the diffraction of the incident radiation, as the wavelength is approximately the magnitude of the interatomic distance, leading to the interference between X-rays reflected in parallel atomic planes as they leave the crystal. Particles scatter incident rays in all directions, but a diffraction pattern will be only obtained if the produced interference is constructive, that is, when Bragg’s Law is satisfied and the scattered beams are in phase (constructive interference when the phase shift is a multiple of 2π). When a monochromatic x-ray beam with wavelength λ is projected onto a crystalline material at an angle θ, constructive interference occurs only when the distance traveled by the rays reflected from successive planes differs by a complete number n of wavelengths according to the Bragg’s law:

\[ n\lambda = 2d_{hkl} \sin \theta \]  
(A.1.1)

or

\[ |\vec{k}_j| = |\vec{k}_j| = \frac{2\pi}{\lambda} \]

\[ \bar{q} = |\vec{k}_j - \vec{k}_j| = 2k, \sin \theta = \frac{4\pi}{\lambda} \sin \theta = \frac{2\pi n}{d} \]  
(A.1.2)

where λ is the wavelength of x-ray, h, k, l are the Miller index used to denote a family of crystalline planes, \(d_{hkl}\) is the interplanar distance in the atomic lattice, θ is the diffraction angle and n is an integer (the order of the reflection). The angle between the diffracted beam and the transmitted beam due to a plane (hkI) is always 2θ, like in Fig. A.1.1, and is specified by the intrinsic interplanar spacing defined by the lattice constant a (\(d_{hkl} = a / \sqrt{h^2 + k^2 + l^2}\)) and the wavelength of the incident x-ray beam.
Fig. A.1.1 (a) Destructive interference of reflected waves: in the reflected waves, maximum and minimum of the wave amplitude are superimposed, because they have an inverse phase. (b) Constructive interference of reflected waves: reflected waves in phase, i.e., maximum are superimposed, the waves satisfy the Bragg’s law.

By varying the angle $\theta$, the Bragg’s law conditions are satisfied by different $d$-spacings in polycrystalline materials. Plotting the angular positions and intensities of the resultant diffracted peaks of radiation produces a pattern, which is characteristic of the sample.

**A.1.1 X-Ray Powder Diffraction Method**

Powder diffraction is a scientific technique using x-ray, neutron, or electron diffraction on powder or microcrystalline samples for structural characterization of materials.

In a powdered sample, ideally, every possible crystalline orientation is equally represented. It is sometimes necessary to rotate the sample to eliminate the effects of texture, that is, the distribution of crystallographic orientations of the sample.

When the scattered radiation is collected on a flat plate detector the different crystalline orientations lead to smooth diffraction rings at different $2\theta$ values around the beam axis rather than discrete spots as observed for single crystal diffraction: as other crystals are added with slightly different orientations, several diffraction spots appear at the same $2\theta$ value and spots start to appear at other values of $2\theta$. Rings consisting of spots and then rings of even intensity are formed. A powder pattern consists of rings of even intensity from each accessible reflection at the $2\theta$ angle defined by Bragg’s Law, that is, the angle between the beam axis and the ring and also called the scattering angle. In accordance with Bragg’s law, each cone of the reflected radiation, and so each ring (see Fig. A.1.2), corresponds to a particular reciprocal lattice vector $G$ in the sample crystal. This leads to the definition of the scattering vector as

$$G = q = 2k \sin \theta = \frac{4\pi}{\lambda} \sin \theta \quad (A.1.3)$$

where all the vectors $k$ of the reciprocal lattice are such that $e^{ik \cdot r} = 1$, and the vector $r$ is the vectors of the direct lattice.
Fig. A.1.2 (a) A powder consists of some tens of randomly oriented single crystals, the diffracted beams are seen to lie on the surface of several cones and so rings of different 2θ values are formed; (b) Image of diffraction rings on a flat plane detector.

Powder diffraction data are usually presented as a diffractogram in which the diffracted intensity is shown as function either of the scattering angle 2θ or as a function of the scattering vector \( q \). The latter variable has the advantage that the diffractogram no longer depends on the value of the wavelength \( \lambda \). The advent of synchrotron sources has widened the choice of wavelength considerably.

The most widespread use of powder diffraction is in the identification and characterisation of crystalline phases present in solids (in a qualitative and quantitative way) each of which produces a distinctive diffraction pattern specific for the crystal family of the specimen. The position of a diffraction peak is entirely determined by the size and shape of the unit cell of the crystalline phase. Each peak represents a certain lattice plane and can therefore be characterized by a Miller index. Both the positions (corresponding to lattice spacings) and the relative intensity of the lines are indicative of a particular phase and material, providing a "fingerprint" that allows a quickly analysis of unknown materials (qualitatively analysis) and to perform materials characterization. Identification is performed by comparison of the diffraction pattern to a known standard or to a database such as the International Centre for Diffraction Data's Powder Diffraction File (PDF) or the Cambridge Structural Database (CSD) that contain all the information about the phase and the lattice parameter. A typical diffraction spectrum consists of a reflected intensity-detected angle (2θ) or reciprocal vector (\( q \)) graph. In contrast to a crystalline pattern consisting of a series of sharp peaks, the random arrangement of atoms in a non-crystalline amorphous materials (liquids, glasses etc.) makes more difficult the constructive interference of the scattered x-rays, resulting in broad, diffuse maxima in the diffraction patterns like in Fig. A.1.3 (b), because the interatomic distances are variable and defined atomic planes don’t exist. The Bragg's ley is rarely satisfied in an amorphous sample and consequently the diffraction peaks can't be distinguished.
A.1.2 Apparatus

An x-ray diffractometer is composed of an x-ray source, a goniometer, a radiation detector and the combined controller and data processor. The x-ray radiation source is usually a vacuum tube, in which electrons are emitted from a cathode by thermoionic effect and impinge violently against an anode under a high electric field. If the electrons have sufficient energy to excite inner shell electrons of the target material, characteristic X-ray spectra are produced in the subsequent electronic decay process. The wavelength of the generated x-rays depend on the type of metal used as the anode (Cu, Fe, Mo, Cr) and the radiation wavelength is between 0.5Å and 2.5Å. The radiation spectra consist of several components, the most important being the $K_α$ and $K_β$ lines. Filtering, by foils or crystal monochromators, is required to produce the monochromatic X-rays needed for diffraction. $K_{α1}$ and $K_{α2}$ lines are sufficiently close in wavelength that a weighted average of the two is used, while the $K_β$ line is lost because it is diffracted in another angle. Copper is the most common target material for single-crystal diffraction, therefore using the Cu $K_α$ radiation ($\lambda = 1.5418Å, E = 8.047$ keV).

The diagram below illustrates the characteristic X-ray emission spectrum obtained from a copper target. It is necessary to arrive at a $\lambda_{min}$ to obtain characteristic lines in the spectrum, and it is inversely proportional to the applied tension of the x-ray tube:

$$E = Ve = h\nu_{min} = h\frac{c}{\lambda_{min}} \quad \text{(A.1.4)}$$

The background and $K_β$ radiation can be reduced by using an absorption filter that cuts off some wavelengths or by a monochromator that works on the principle of diffraction.
whose angular position 2 special slits which define and collimate the incident and diffracted beams, pattern is recorded with a photographic film or a radiation counter. B and C are and is diffracted in a characteristic manner by the sample to form a convergent on the target emerges from the X-ray tube through a collimator, hits the sample, perpendicular to the plane of drawing. The primary beam in the line focal spot form of a flat plate, is mounted on a table which can be rotated around an axis a typical configuration of a diffraction system. A polycrystalline sample, in the line of traditional generators is relatively low, requiring large exposure times and precluding any time dependent measurement. The advent of synchrotron sources has drastically changed this picture and caused powder diffraction methods to enter a whole new phase of development. The general features of a diffractometer are shown in Fig. A.1.5 that illustrates a typical configuration of a diffraction system. A polycrystalline sample, in the form of a flat plate, is mounted on a table which can be rotated around an axis perpendicular to the plane of drawing. The primary beam in the line focal spot on the target emerges from the X-ray tube through a collimator, hits the sample, and is diffracted in a characteristic manner by the sample to form a convergent diffracted beam. This beam is focused through the slit C and the diffraction pattern is recorded with a photographic film or a radiation counter. B and C are special slits which define and collimate the incident and diffracted beams, respectively. The X-ray receiving slits and counter are supported on a carriage whose angular position 29 can be recorded on the graduated scale goniometer G. A detector records and processes this X-ray signal and converts the signal to

<table>
<thead>
<tr>
<th>Element</th>
<th>Kα (weight average)</th>
<th>Kα2 (strong)</th>
<th>Kα1 (very strong)</th>
<th>Kβ (weak)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>0.229100</td>
<td>0.229361</td>
<td>0.228970</td>
<td>0.208487</td>
</tr>
<tr>
<td>Fe</td>
<td>0.193736</td>
<td>0.193998</td>
<td>0.193604</td>
<td>0.175661</td>
</tr>
<tr>
<td>Co</td>
<td>0.179026</td>
<td>0.179285</td>
<td>0.178897</td>
<td>0.162079</td>
</tr>
<tr>
<td>Cu</td>
<td>0.154184</td>
<td>0.154439</td>
<td>0.154056</td>
<td>0.139222</td>
</tr>
<tr>
<td>Mo</td>
<td>0.071073</td>
<td>0.071359</td>
<td>0.070930</td>
<td>0.063229</td>
</tr>
</tbody>
</table>

**Tab. A.1.1** Different wavelengths produced by each target are given in the table. The wavelength in nm varies for each source. The most commonly used laboratory X-ray tube uses a Copper anode, but Cobalt and Molybdenum are also popular.

In house applications of X-ray diffraction has always been limited to the relatively few wavelengths shown in the above table. Another limitation is that the intensity of traditional generators is relatively low, requiring large exposure
a count rate which is then output to a device such as a printer or a computer monitor.

![Schematic diagram of x-ray diffractometer.](image)

**Fig. A.1.5** Schematic diagram of x-ray diffractometer. T, x-ray tube target; B and C, slit and collimator assemblies; S, sample holder; D, x-ray detector; G, goniometer scale graduated in degrees.

The goniometer is an angle scanning apparatus for adjusting two angles, that between the x-ray beam and the specimen surface and that between the specimen surface and the detector.

Diffractometers can be operated both in transmission and reflected configuration. The reflection one is the most common. The powder sample is filled in a small container and its surface carefully flattened. The container is placed on one axis of the diffractometer and tilted by an angle $\theta$ while a detector rotates around it on an arm to collect the diffracted x-rays at twice this angle, that is $2\theta$. This configuration is known under the name Bragg-Brentano. The distance from the x-ray focal spot and the sample is the same as from the sample to the detector. If we drive the sample holder and the detector in a 1:2 relationship, the reflected (diffracted) beam will stay focused on the circle of constant radius and the detector, moving on this circle, will always be measuring.

For the $\theta$-2$\theta$ goniometer, the x-ray tube is stationary, the sample moves by the angle $\theta$ and the detector simultaneously moves by the angle 2$\theta$. For typical powder patterns, data is collected at 2$\theta$ from $-5^\circ$ to $70^\circ$, angles that are preset in the X-ray scan. The **Fig. A.1.6** shows this type of goniometer.
Fig. A.1.6 (a) Bragg-Brentano $\theta - 2\theta$ setup; (b) Goniometer with x-ray tube and the detector.

Another configuration is the $\theta - \theta$ goniometer in which the sample is stationary in the horizontal position while both the x-ray tube and the detector are rotated simultaneously around it over the angular range $\theta$. The angle formed between the tube and the detector is $2\theta$. This configuration is most convenient for loose powder.

The x-ray diffraction made with a synchrotron source operates in a transmission configuration and the intensity of the peaks is a function of the reciprocal vector $q$ instead of the angle $2\theta$. 
A.2 Scanning Electron Microscopy (SEM)

The Scanning Electron Microscope (SEM) is an electronic microscope that creates an image by focusing a high energy beam of electrons onto the surface of a sample and detecting signals from the interaction of the incident electrons with the surface of the sample. The type of signals gathered in a SEM varies and can include secondary electrons, characteristic x-rays, and back scattered electrons. The SEM is capable of producing high-resolution images of a sample surface and secondary electron images that have great depth of field and great resolution. Characteristic x-rays are emitted when the primary beam causes the ejection of inner shell electrons from the sample and are used to determine the elemental composition of the sample. The back-scattered electrons emitted from the sample may be used alone to form an image or in conjunction with the characteristic x-rays as atomic number contrast clues to the elemental composition of the sample.

![SEM Equipment](image)

**Fig. A.2.1** Equip of SEM formed by: sample chamber; vacuum system; electron gun; the column; commands and TV screens.

In a typical SEM, the scanning electron beam is produced in an electron microscope column. Electrons are thermionically emitted in the superior part of the microscope from a tungsten or lanthanum hexaboride (LaB$_6$) cathode (or field emission cathode) and are accelerated by a potential difference with an anode. The electron beam, which typically has an energy ranging from a few hundred eV to 100 keV, follows a vertical trajectory inside the microscope column and it is focused by one or two electromagnetic lenses into a beam with a very fine focal spot. The beam passes through pairs of $x$-$y$ magnetic scanning coils or pairs of deflector plates arranged perpendicular to one other in the electron optical column between the two magnetic lenses, which deflect the beam horizontally and vertically so that it scans over a rectangular area of the sample surface. The amplification of the SEM is produced simply by electronically varying the deflection angle of the scanning electron beam. When the primary electron beam interacts with the sample, the electrons lose energy by repeated scattering and absorption within a peardrop-shaped volume of the specimen known as the interaction volume, which extends from less than 100 nm to around 5 µm into the surface (see **Fig. A.2.4**). The size of the interaction
volume depends on the electron landing energy, the atomic number of the specimen and its density. The energy exchange between the electron beam and the sample results in the emission of electrons and electromagnetic radiation, which can be detected to produce an image. The detectors collect the secondary electrons and the different energies are converted in a tension that, amplified, can be converted to an image suitable to be shown in an optical display, usually a TV screen. The image consist of many points of different intensity correspondig at the sample topography; its electron beam is scanned synchronously with the primary probing beam of the microscope column, that is both beams are controlled by the same scanning electronics and the amplification of the SEM is adjusted by a scaling factor.

In the SEM the measure of the scanned zone is variable and it can be reduced or increased. The samples location is inside a chamber on some supports covered with a sticky layer on which the samples (like pieces of ribbons in Fig. A.2.3) are placed. These supports are earthed in order to avoid the electrically charge of the samples due to the incident electrons.

Fig. A.2.2 Schematic set-up of a SEM.
Fig. 5.2.3 *Samples deposition inside the chamber.*

The measures are made with a vacuum pressure of the order of $10^{-10}$ bar inside the sample chamber to avoid the interference between the air molecules and the sample.

**A.2.1 Detection of secondary electrons**

Secondary electrons (SE) are electrons generated as ionization products when an incident particle (often charged particles such as electrons or ion or photons) impacts the material with sufficient high energy (typically 2-10 keV). They are called 'secondary' because they are emitted from the surface of a material with a very low energy compared with the incident beam, being its energy in the range between 0 and 50 eV.

SE are generated by an inelastic collision between an electron of the primary beam and the sample, transferring part of its energy to an electron of a sample atom. As a consequence of this energy loss, the primary electron changes its trajectory causing more collisions and, thus, other electron leave the atom with a very low kinetic energy (< 50 eV). Every incident electron can generate various secondary electrons because they have undergone multiple scattering events on their way. Their spectral distribution and their intensity is thus not very specific to a particular material.

Due to their low energy, these electrons originate within a few nanometers from the surface, from a zone bigger than the impact beam one. The most common imaging mode monitors low energy (< 50 eV) secondary electrons, and due to the lack of forward scattering, less shadowing is observed and variations in surface roughness are made visible. A good insight into the geometry of an object or a surface can be achieved by using different detectors and different irradiation geometry. The formation of a topographical image is due to local variations of the electron emissivity of the surface. The brightness of the signal depends on the number of secondary electrons reaching the detector.

A characteristic of the emitted low-energy SE is that they have a small escape depth and have a great spatial resolution, and thus carry information from the small, narrow neck of the "pear", as we can see in fig.. If the beam enters the sample perpendicular to the surface, then the activated region is uniform about the axis of the beam and a certain number of electrons escape from within the
sample. As the angle of incidence increases, the escape distance of one side of the beam will decrease, and more secondary electrons will be emitted. Thus steep surfaces and edges tend to be brighter than flat surfaces, which results in images with a well-defined, three-dimensional appearance. The spatial resolution of the SEM depends on the size of the electron spot, which in turn depends on both the wavelength of the electrons and the magnetic electro-optical system which produces the scanning beam. The resolution is also limited by the size of the interaction volume, or the extent which the material interacts with the electron beam. Both the spot size and the interaction volume might be large compared to the distances between atoms, so the resolution of the SEM is not high enough to image individual atoms, but resolutions of 1 nm are possible.

![Diagram of electron probe interaction](image)

**Fig. A.2.4** Schematic overview of the pear-shaped volume probed by different microprobe signals (electron and x-ray emission), when a primary electron beam is incident on the surface: much better resolution is obtained by the Auger probe but the x-ray probe offers better depth analysis.

### A.2.2 Detection of backscattered electrons

Backscattered electrons (BSE) consist of high-energy electrons originated by an elastic collision between the sample and the electron beam, that are reflected or back-scattered out of the specimen interaction volume. The energy interchange in these collisions is minimum, so the detected electrons have an high kinetic energy but with a change in the momentum with respect the incident electrons, that is a change in the direction of the velocity vector. The resolution obtained with this technique is small because of the large emission area. There are less backscattered electrons emitted from a sample than secondary electrons. Backscattered electrons may be used to detect contrast between areas with different chemical compositions and obtain compositional information, especially when the average atomic number of the various regions is different: the sensibility in the chemical local composition and so the product efficiency of
BSE increases with the atomic number $Z$ of the elements because the probability that an electron is backscattered increases with the atomic number. So the brightness of the BSE image is function of the composition and tends to increase with the atomic number.

### A.2.3 Analytic Method

X-rays, which are also produced by the interaction of electrons with the sample, may also be detected in a SEM equipped for Energy Dispersive X-ray Spectroscopy (EDS or EDX). This method is used for the elemental analysis or chemical composition of a specimen volume. It is a technique of chemical microanalysis that analyzes x-rays emitted by the matter when it is excited by the electron beam. Its characterization capabilities are due in large part to the fundamental principle that each element of the periodic table has a unique atomic structure allowing x-rays that are characteristic of an element to be uniquely distinguished from each other.

To stimulate the emission of characteristic x-rays from a specimen, an high energy beam of charged particles such as electrons is focused into the sample to be characterized. The atoms within the sample are in the ground state (or unexcited) with electrons situated in discrete energy levels or electron shells. The incident beam may excite an electron in an inner shell, prompting its ejection and resulting in the formation of an electron hole within the atomic electronic structure. An electron from an outer, higher-energy shell then fills the hole, and the difference in energy between the higher-energy shell and the lower energy shell is released in the form of an x-ray, like in Fig. A.2.5. The x-ray released by the electron is then detected and analyzed by the energy dispersive spectrometer. These x-rays are characteristic of the difference in energy between the two shells, and of the atomic structure of the element from which they are emitted.

![Fig. A.2.5 Schematic view of the principle of x-ray excitation due to the electron-hole coupling in the electron shells of an atom.](image-url)
EDS systems are most commonly found on scanning electron microscopes. The x-ray detector of EDS measure the number of x-rays as a function of the energy that is characteristic of each element; the signal is converted to a voltage pulse by a preamplifier and this signal is further amplified and shaped by a pulse processor before being displayed and passed to an analyzer for data display and analysis. Therefore, a spectrum of the x-ray energy of all the elements is obtained, thus giving a qualitative and quantitative determination of the elements present in the examined volume. The intensity or area of a peak in an EDS spectrum is proportional to the concentration of the corresponding element in the specimen. For determining elemental content, the electron-beam current is assumed to be uniform throughout the specimen.

Fig. A.2.6 Example of typical EDX spectrum for a 47nm specimen of NiO on a 200-mesh Mo grid with the 200 keV incident beam near the centre of a grid square: by looking at the characteristic elemental peaks an elemental mapping is possible by analysing the sample point by point.
A.3 Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry or DSC is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and a reference is measured as a function of temperature. Both sample and reference are maintained at nearly the same temperature throughout the experiment. Generally, the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time, although a constant temperature program is also common. The reference sample should have a well-defined heat capacity over the range of temperature to be scanned.

In the power-compensation DSC, Fig. A.3.1, the sample and the reference holders are placed in separated but identical furnaces and their temperature are controlled independently. The sample and the reference are maintained at the same temperature by varying the power supply, that is to keep the value of $\Delta T$, the temperature difference between the two furnaces, equal to zero by placing the temperature sensors, Pt resistance thermometers, into a bridge circuit. The energy required to maintain this zero temperature difference is indicative of the enthalpy change in the sample in comparison to the reference: the power needed to keep the bridge circuit in balance is proportional to the change in heat capacity or enthalpy.

The basic principle underlying this technique is the excess or defect of heat flow that is needed to maintain the same temperature at the reference and the sample when it undergoes a physical transformation such as phase transitions. Whether more or less heat must flow to the sample depends on whether the process is exothermic or endothermic. For example, as a solid sample melts it will require more heat flowing to increase its temperature at the same rate as the reference. This is due to the absorption of heat by the sample as it undergoes the endothermic phase transition from solid to liquid. Likewise, as the sample undergoes exothermic processes (such as crystallization) less heat is required to raise the sample temperature. By observing the difference in heat flow between the sample and reference, differential scanning calorimeters are able to measure the amount of heat absorbed or released during such transitions. DSC may also be used to observe more subtle phase changes, such as glass transitions because they are reflected in a change in the heat capacity.
A.3.1 DSC curves

Differential scanning calorimetry determines the temperature and heat of transformation and can be used to measure a number of characteristic properties of the sample, like phase changes, glass transition, melting, purity, evaporation, sublimation, crystallization, pyrolysis, heat capacity, polymerization, denaturation / aggregation, compatibility, etc. The result of a DSC experiment is a curve of heat flux versus temperature or versus time, that is the computer plots the heat absorbed by the sample against temperature. From this analysis can be obtained:

\[
\frac{q}{t} = \text{heat flow};
\]
\[
\frac{\Delta T}{t} = \text{heating rate};
\]
\[
\frac{q}{\Delta T} = c_p
\]

where \( q \) is the unit of heat, \( t \) is the unit time, the heating rate is temperature increase \( \Delta T \) per unit time \( t \), and \( c_p \) is the heat capacity, that is obtained dividing the amount of heat supplied to get a certain temperature increase by the resulting temperature increase.

We can describe a typical DSC curve as the temperature in a solid is increased. At the beginning structural relaxation or a glass transition may occur as the temperature of the solid is increased. These transitions appear as a step in the baseline of the recorded DSC signal because the sample is undergoing a second order transition, that is, a thermal transition that involves a change in heat capacity but does not have a latent heat; no formal phase change occurs, only the state of motion is changing during the transition. Because of this change in the heat capacity at the glass transition, we can use DSC to measure the glass transition temperature. The change does not occur suddenly, but takes place over a temperature range, therefore the value of \( T_g \) can have an uncertainty depending on the way it is computed. If the solid under study is not amorphous there are no changes in the slope of the DSC curves at these first stages.

As the temperature increases, the solid will become less viscous and have a lot of mobility. At some point the molecules or atoms may obtain enough freedom of motion to spontaneously arrange themselves into a crystalline form. This is known as the crystallization temperature (\( T_c \)). This transition from solid to crystalline is an exothermic process, thus the sample release heat. The area below the peak is the latent energy of crystallization.

As the temperature further increases the sample eventually reaches another thermal transition at the melting temperature (\( T_m \)). The melting process results in an endothermic peak in the DSC curve, therefore the heater under the sample has to release a lot of heat into the sample in order to both melt the crystals and keep the temperature rising at the same rate as in the reference.
The crystalization and the melting are first order transition, that is, a thermal transition that involves both a latent heat (the temperature does not change until the transition is completed) and a change in the heat capacity.

![Diagram of DSC curve showing glass transition, crystallization peak, and melting peak.](image)

**Fig. A.3.2** Characteristics of a DSC curve: (a) Glass transition; (b) Crystallization peak (exothermic); (c) Melting peak (endothermic).

The calculation of enthalpies of transitions from DSC curves is done by integrating the peak corresponding to the given transition. It can be shown that the enthalpy of transition $\Delta H$ can be expressed using the equation:

$$\Delta H = KA$$  \hspace{1cm} (A.3.2)

where $K$ is the calorimetric constant and $A$ is the area under the curve. The calorimetric constant will vary from instrument to instrument, and can be determined by analyzing a well-characterized sample with known enthalpies of transition.