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**The physical and chemical mechanisms  
behind wine induced superconductivity  
in  $\text{FeTe}_{0.9}\text{Se}_{0.1}$**

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# 1 Details

## 1.1 Details of proposal

Title: The physical and chemical mechanisms behind wine induced superconductivity in  $\text{FeTe}_{0.9}\text{Se}_{0.1}$

Area: Condensed matter physics

Keywords: Iron-based superconductor,  $\text{FeTe}_{0.9}\text{Se}_{0.1}$ , red wine treatment, superconductivity, alcoholic beverages, wine-induced superconductivity, type-II superconductor, chemical induction of superconductivity.

## 1.2 Details of applicants

Bryan Advocaat	Mathematics	Male
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## 2 Abstracts

### 2.1 Abstract for scientists

Ever since the discovery of the first iron-based superconductor [1], scientists have searched for iron based superconductors with higher critical temperatures and higher critical currents. However the origin of superconductivity in these superconductors with generally anti-ferromagnetic parent compounds is still unclear. In the past years, much effort has been made by scientists to understand their electron pairing mechanisms and energy gap symmetry [2, 3, 4]. Among these superconductors are  $\text{FeTe}_{1-x}\text{S}_x$  [5] and  $\text{FeTe}_{1-x}\text{Se}_x$  [6]. It is known that excess iron in these iron-based superconductors suppresses their superconductivity and that submerging in wine induces superconductivity by removing excess iron ions from the lattice, a process called deintercalation [7]. However, custom made solutions have never reached the effects wine has on the superconductivity. It is thus suggested that more processes take place to enhance superconductivity.

In the proposed research, the physical and chemical changes of  $\text{FeTe}_{1-x}\text{Se}_x$  induced by submerging in wine will be studied. In particular it will be investigated if the induced superconductivity can be reversed. By doing so a better understanding of the reactions resulting in the deintercalation of excess iron and the origin of the enhanced superconductivity will be achieved. Ultimately, this will help better understand the magnetic pairing mechanisms and structural changes which can be made to materials to enhance superconductivity.

### 2.2 Abstract for broad scientific committee

Ever since the discovery of the first iron-based superconductor [1], scientists have searched for iron based superconductors with higher critical temperatures and higher critical currents. However the origin of superconductivity in these superconductors is still unclear. In the past years, much effort has been made by scientists to understand the characteristics of materials which exhibit superconductivity. Among these superconductors are  $\text{FeTe}_{1-x}\text{S}_x$  [5] and  $\text{FeTe}_{1-x}\text{Se}_x$  [6]. It is known that excess iron atoms in the crystals of these iron-based superconductors suppresses their superconductivity and that submerging in wine induces superconductivity by removing excess iron ions from the lattice. However, custom made solutions have never reached the effects wine has on the superconductivity. It is thus suggested that more processes than only the removal of excess iron enhance superconductivity.

In the proposed research, the physical and chemical changes of  $\text{FeTe}_{1-x}\text{Se}_x$  induced by submerging in wine will be studied. In particular it will be investigated if the induced superconductivity can be reversed. By doing so a better understanding of the reactions resulting in the partial removal of excess iron ions from the lattice of excess iron and the origin of the enhanced superconductivity will be achieved. Ultimately, this will help better understand the changes which can be made to materials to enhance superconductivity.

## 2.3 Abstract for general public

Supergeleiders hebben veel aandacht onder wetenschappers op dit moment. Dit komt door de enorm sterke stroom die erdoorheen kan gaan zonder dat deze stroom energie kost. Met kamertemperatuur supergeleiders zou elektriciteit kosteloos over de hele wereld verspreid kunnen worden. Echter, huidige supergeleiders werken alleen bij extreem lage temperaturen.

Het is bekend dat verwarmen van het kristal  $\text{FeTe}_{1-x}\text{Se}_x$  in zijn supergeleiding versterkt. In het voorgestelde onderzoek zal naar de reden hiervoor worden gezocht. Hiermee zal tevens meer duidelijk worden over de manieren waarop supergeleiding kan worden versterkt in andere supergeleiders en zo aan een beter begrip van supergeleiding bijdragen.

### 3 Introduction

In the early 20th century the Dutch physicist Heike Kamerlingh Onnes first made a superconducting material using liquid helium to cool down Mercury to 3K [8]. During the 20th century more superconductors with higher critical temperatures were found. Much later, in 2008, the first iron based superconductor was found [1] and many more iron based superconductors have been discovered since. Because iron has very different magnetic properties than earlier found high temperature superconductors based on copper oxides, a lot of attention was drawn to iron based superconductors to find theories which could explain high temperature superconductivity. These superconductors commonly have a layered, tetragonal or orthorhombic structure [9]. Among these superconductors are  $\text{FeTe}_{1-x}\text{S}_x$  [5] and  $\text{FeTe}_{1-x}\text{Se}_x$  [6].

It was found that oxygen annealing induces superconductivity in  $\text{FeTe}_{0.8}\text{S}_{0.2}$ . During annealing a material is exposed to high temperatures in a certain atmosphere, for example oxygen in the case of oxygen annealing. Annealing afterwards in vacuum reversed this effect over time [10]. In 2010 it was found that superconductivity in  $\text{FeTe}_{0.8}\text{S}_{0.2}$  can be enhanced by submerging the superconductor in alcoholic beverages for 24 hours at 70°C [11]. After further research, it appeared that excess iron in  $\text{Fe}_{1+d}\text{Te}_{1-x}\text{S}_x$  suppressed superconductivity and that removal of these excess iron ions, called deintercalation, by submerging the sample in alcoholic beverages induced superconductivity [7]. In  $\text{FeTe}_{0.9}\text{Se}_{0.1}$  a similar effect was observed after submerging in wine. Reproduced from the data in [12], a correlation of 0.910 (by PMCC (Pearson product-moment correlation coefficient)) has been found between the dissolved excess iron in the wine from  $\text{FeTe}_{0.9}\text{Se}_{0.1}$  after submerging and the shielding volume fraction of the sample. The shielding volume fraction of a sample is defined as the proportion of an applied external magnetic field which is expelled from the material. Any sample which has a superconducting surface will expel all magnetic fields, which is called the Meissner effect [13]. Type-II superconductors are partially superconducting and contain magnetic vortices which do allow magnetic fields to partially pass through the material. For such superconductors it is thus common to define the shielding volume fraction as a measure for the superconductivity of the sample.

A correlation of  $-0.861$  (by PMCC) has been found between the pH of the alcoholic beverage and the shielding volume fraction as well reproduced by the data from [12]. Further research by Deguchi et al. indicated a positive correlation between the shielding volume fraction and the concentration of various organic acids present in the alcoholic beverages used [7, 14].

However the actual reactions causing deintercalation of excess iron, the possible presence of other reactions causing enhanced superconductivity and incompleteness of the correlations mentioned above are still not clarified. The most important example of an alternate reaction can be found based on the effects of oxygen annealing of  $\text{FeTe}_{1-x}\text{Se}_x$ . Oxygen annealing causes suppression of the magnetic properties of the excess interlayer iron without deintercalation and this effect is reversible by placing the superconductor in vacuum [15].

### 4 Research Question

Which physical or chemical processes during the submerging of  $\text{FeTe}_{0.9}\text{Se}_{0.1}$  in wine induce superconductivity other than deintercalation of excess iron?

## 5 Scientific Background

### 5.1 Crystal Structure

One of the simplest layered iron-based superconductors is  $\text{FeTe}_{1-x}\text{Se}_x$  [16]. This superconductor consists of layers which have a tetragonal structure of iron atoms with tellurium or selenium atoms in the centre, slightly shifted in the direction perpendicular to the plane, as shown in figure 1.

The parent compound,  $\text{FeTe}$ , is not superconducting and to induce superconductivity, the tellurium is partially replaced with sulphur or selenium. Weak superconductivity in  $\text{FeTe}_{1-x}\text{Se}_x$  is found starting at  $x = 0.1$ . At a value of  $x = 0.5$  bulk superconductivity occurs in as-grown samples.

During the synthesis of the layered  $\text{FeTe}_{1-x}\text{Se}_x$  crystals, excess iron atoms will be incorporated in between the layers. This excess iron has a valence close to one, donating electrons to the superconducting layers. The extra electrons and the presence of a charged iron atom disturbs the magnetic properties of the crystal layers and suppresses its superconducting properties [17]. However excess iron will naturally be present in both monocrystalline and polycrystalline samples of  $\text{FeTe}_{1-x}\text{Se}_x$  and to induce superconductivity the effects of this excess iron will have to be cancelled out or the excess iron will have to be deintercalated.

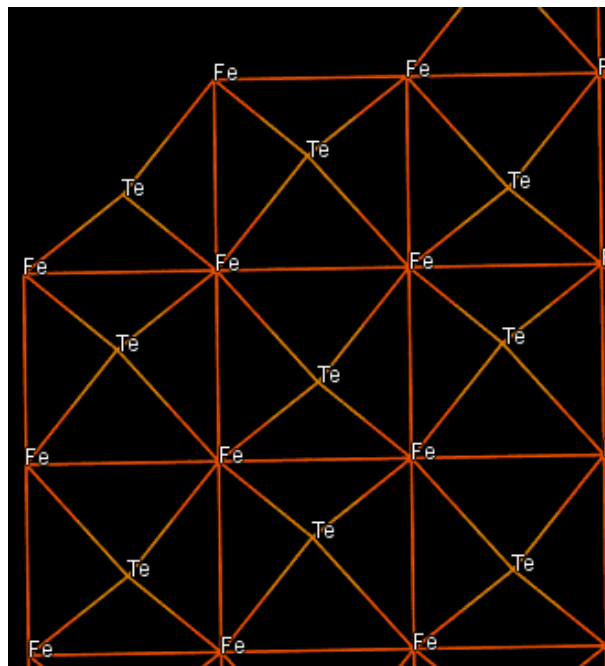


Figure 1: One layer of  $\text{FeTe}$ . The Te atoms are alternatingly pointing upwards and downwards [18]. In  $\text{FeTe}_{1-x}\text{Se}_x$ , part of the tellurium atoms are substituted by selenium.

## 5.2 Oxygen and Pnictogen Annealing

One method that has been found to enhance the superconductivity in  $\text{FeTe}_{1-x}\text{Se}_x$  at  $x$  lower than 0.5 is oxygen annealing. It was found that by sealing the crystal in a volume filled with oxygen that the shielding volume fraction of  $\text{FeTe}_{1-x}\text{Se}_x$  was increased [15]. In figure 2 the relation between the  $x$ -value and the maximum induced shielding volume fraction by oxygen annealing is shown for  $\text{FeTe}_{1-x}\text{Se}_x$ . It can be seen that for values of  $x \geq 0.1$  oxygen annealing enhances the shielding volume fraction to almost 100 %. A very likely explanation for these results is that the oxygen atoms intercalate between the layers of the crystal and compensate for the anti-ferromagnetic effects of the excess iron atoms [15]. Superconductivity induced by oxygen annealing is present in the bulk of the material and not only at the surface.

Not only has  $\text{FeTe}_{1-x}\text{Se}_x$  been annealed with oxygen, it has also been annealed with pnictides<sup>1</sup>, namely phosphorus, arsenic and antimony. All of those induced, just as with oxygen annealing, bulk superconductivity in the crystals. Not all three elements had the same optimal annealing temperature or concentration which can be explained by the differences in the saturated vapour pressures. It has also been suggested that phosphorus acts as a catalyst for a reaction of the excess iron to form  $\text{FeTe}_2$ . In contrast, it was suggested that arsenic interacts in two ways with the excess iron. On the one hand that it acts as a catalyst for the formation of  $\text{FeTe}_2$ , similar to phosphorus, on the other hand it appears to react directly with the excess iron. Both cases, however, result in a decrease in excess iron and thus in an increase in shielding volume fraction [19]. Annealing with  $\text{I}_2$  also induces superconductivity, but only at the surface. A possible explanation for the fact that  $\text{I}_2$  only induces it at the surface might be that the  $\text{I}_2$  molecules are too large to intercalate between the layers of the crystal and therefore can only deintercalate the excess iron near the surface of the crystal [20].

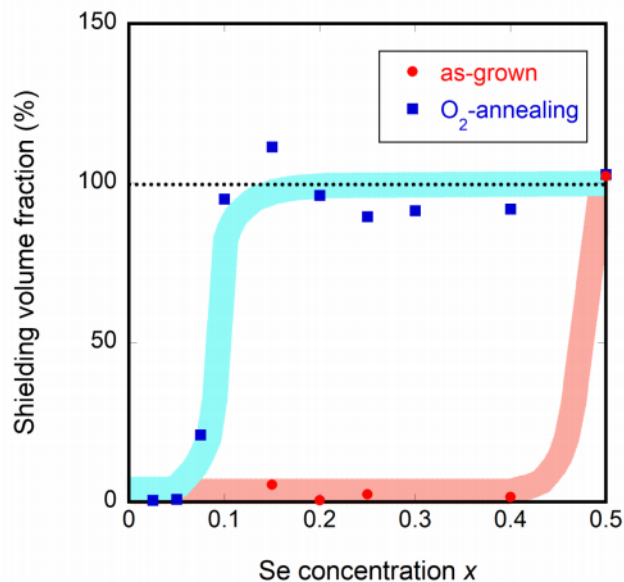


Figure 2: The shielding volume fraction as a function of the Se fraction ( $x$ ) in  $\text{FeTe}_{1-x}\text{Se}_x$ , both for the as-grown crystals and for the crystals annealed with oxygen [15].

<sup>1</sup>Elements from group 15 of the periodic table



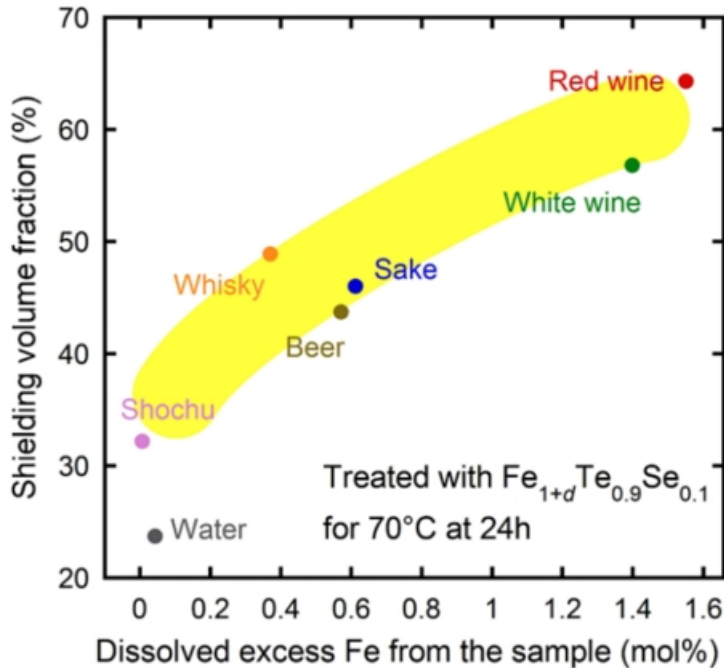


Figure 3: The shielding volume fraction as a function of the amount of excess iron measured in the samples. Next to the measure points are the names for the specific alcoholic beverage used in that case [12].

### 5.3 Enhanced superconductivity by alcoholic beverages

Besides the already mentioned ways to enhance superconductivity in  $\text{FeTe}_{1-x}\text{Se}_x$ , there is another surprising method to do so, namely submerging the crystal in alcoholic beverages. Deguchi et al. [12] have submerged  $\text{FeTe}_{1-x}\text{Se}_x$  crystals into several different alcoholic beverages (red wine, white wine, beer, sake, shochu and whiskey) and measured an increase in the shielding volume fraction. The highest shielding fraction volume after submerging was found in red wine, as can be seen in figure 3.

After submerging the crystals in the different alcoholic beverages the amount of excess iron in the liquids was measured alongside the shielding volume fraction. Deduced from figure 3, the results show a clear correlation between these two properties. This correlation (by PMCC) is 0.910, or 0.933 when the value of the water sample is dismissed. This correlation is rather high so indeed suggests that it is very likely that the alcoholic beverages deintercalate excess iron from the crystal. However, the correlation is not high enough to conclude that that is the only cause of the enhanced superconductivity. Furthermore, shochu enhances the superconductivity, however no excess iron was measured in the shochu after the submerging. Both of these reasons suggest other reactions taking place than just the deintercalation of excess iron. Also an anti-correlation between the shielding volume fraction and the pH of the alcoholic beverages was measured. This might suggest for example that  $\text{H}^+$  atoms interact directly with the excess iron or that  $\text{H}^+$  plays a crucial role in reactions causing the deintercalation of excess iron [12].

To find out which other components in wine are responsible for the increase in the superconductivity, Deguchi et al. also submerged the crystal in multiple acids present in wine and found positive correlations by PMCC with the shielding volume fraction. The correlation with tartaric acid was 0.642, with  $\beta$ -alanine 0.947, with citric acid 0.675 and with malic acid 0.907. All of these acids enhanced the superconductivity and an increase in iron in these acids was measured after the submerging. Thus it seems likely that these acids can deintercalate excess iron in the crystal. However these acids did not increase the shielding volume fraction as much as the wines, therefore suggesting that there are other components responsible for the enhanced superconductivity [7].

The enhanced superconductivity of the crystal was measured to be only a surface effect [20]. This might be explained by the fact that the molecules responsible for the increase in shielding volume fraction are too large to enter the crystal. For example the acids which are likely to deintercalate excess iron, cannot enter the crystal and thus only deintercalate the excess iron near the surface.

In another iron layered crystal,  $\text{FeTe}_{1-x}\text{S}_x$ , which is somewhat similar to  $\text{FeTe}_{1-x}\text{Se}_x$ , it was also found that alcoholic beverages enhance superconductivity [11]. This might suggest that the enhancement in shielding volume fraction by alcoholic beverages is a general characteristic for this type of superconducting crystals [12].

## 6 Methodology

The goal of this research project is to find out how the submerging of  $\text{FeTe}_{0.9}\text{Se}_{0.1}$  in red wine enhances its shielding volume fraction. To describe the research, first an outline of the main experiment will be given. Then it will be explained which types of reactions are expected to occur and how they can be investigated. This will be followed by an explanation of the measurement methods and why they are well suited to give the required information.

### 6.1 Outline

In this experiment we expect that next to iron deintercalation other effects will be found that enhance the superconductivity in  $\text{FeTe}_{0.9}\text{Se}_{0.1}$ . In the papers by Deguchi et al. [7, 11, 12] there are multiple correlations found between the concentration of a certain substance and the shielding volume fraction caused by submerging  $\text{FeTe}_{1-x}\text{Se}_x$  or  $\text{FeTe}_{1-x}\text{S}_x$  in alcoholic beverages. None of these however seem to explain why wine is so particularly good at enhancing the superconductivity, because the correlation coefficients are lower than 0.95. Also the results that were found by using pure solutions in water had a substantially smaller effect. To determine which processes induce superconductivity during submerging in wine of  $\text{FeTe}_{0.9}\text{Se}_{0.1}$  other than de-intercalation of excess iron, it needs to be determined if there are substances that enter the crystal. With oxygen annealing this is the case and therefore it is to be expected that other substances from the wine could also enter the crystal, which can either settle all over the crystal or only enter the surface. It is known that the induction of superconductivity is observed mainly at the surface [21] which suggests that the responsible pathways differ for the surface and the bulk. Single crystal samples will be used for the measurements because then the bulk can be clearly distinguished from the surface. This can provide more insight into the reaction mechanisms that are present. Also polycrystalline samples will be used to be able to compare the results to previous studies [7, 11, 12].

Some of the molecules which entered the crystal might be able to leave the crystal again. This was observed for oxygen by Y. Mizuguchi et al. [10]. Therefore it is interesting to find which of the other molecules can leave the crystal. This will be done by what will be referred to as reverse annealing, which is submerging the superconductor in water and after that putting it in vacuum. This way the substances that are able to leave the crystal will do so. This potentially leaves some substances that are not able to leave the crystal, behind. To find the substances that left the crystal, the water and gases from the reverse annealing will be examined. To find the substances that were potentially left behind the crystal itself will be examined to find those foreign substances. It is also possible that the crystal structure changes during the submerging of the superconductor in wine, therefore the structure will be closely monitored between the different steps to find those potential changes in crystal structure. To monitor the superconductivity the shielding volume fraction will be measured between the steps of the experiment. By measuring the shielding volume fraction after every step it can be determined what part of the superconductivity is a result of foreign substances in the crystal that are able to leave via reverse annealing.

## 6.2 Expected reaction types

During the submerging of the sample in ample red wine, a combination of several reactions might occur. In this section it will be attempted to categorise these reactions into four reaction types. Each of these types can then separately be investigated with well chosen experiments and measurements with which their relative contribution to the enhancement of the superconductivity can be determined. The knowledge of the structure of the substances involved in the reaction in conjunction with the reaction type should allow either a decent understanding of the reaction that occurred or the devising of several reaction pathways, which can be tested in follow-up research.

The first reaction type consists of atoms leaving the crystal during the submerging in wine. It is known that this reaction type occurs and plays a role in inducing superconductivity in the crystal, since iron deintercalation falls in this category. In the second and third types atoms or molecules enter the crystal. The difference between the types is the way these molecules bind in the crystal. When the molecules or atoms react according to the second type, they will leave the crystal when the crystal is subjected to an appropriate medium that lacks these molecules or atoms. This is referred to as annealing, and is known to occur when  $\text{FeTe}_{0.9}\text{Se}_{0.1}$  is subjected to  $\text{O}_2$ , for example [22]. The third type consists of the atoms or molecules that enter the crystal that do not react according to the second type. Even though such reactions have not yet been determined, it is conceivable that these reactions will occur when  $\text{FeTe}_{0.9}\text{Se}_{0.1}$  is subjected to a liquid with a vast array of molecules, such as wine, especially for molecules that chemically react with the crystal. The last type is a reaction that causes a change in the crystal structure of the crystal without molecules entering. It is likely that all of the other types of reactions will also involve a change in the crystal structure, but it is still important to keep track of the crystal structure of the sample, because the precise crystal structure plays a key role in superconductivity.

## 6.3 Investigating the separate reaction types

This research project will concentrate on reactions of type two and three. For studies of iron deintercalation, the only type one reaction, the reader can refer to [12]. The changes to the crystal structure, reaction type four, will be monitored, but this knowledge will mainly be used to give an indication of the amount of influence certain reactions had on the crystal.

To reach scientific conclusions on reaction types two or three separately, the influences from these reaction types have to be separated. This will be done by putting the crystal in ultrapure water for 24 hours at  $70^\circ\text{C}$  and then in vacuum for 24 hours at  $70^\circ\text{C}$ , which is referred to as reverse annealing. This allows all the molecules that react according to type two to leave the crystal again, since they are all water soluble, because they were dissolved in wine. The vacuum then makes all the small molecules that are left leave the crystal, especially the water that might have entered the crystal and for example oxygen. The molecules or atoms that react in a type three fashion can however not leave the crystal. Therefore this process separates the type two atoms and molecules from the type three ones. This makes it possible to see which atoms and molecules can undergo a type two reaction by investigating the water and the gases that were released when the sample was in the vacuum. By determining the molecules and atoms that are still in the crystal, the atoms and molecules that can undergo a type three reaction can also be determined.

Additionally, it is useful to know how far into the crystal the molecules and atoms can react to determine plausible reaction mechanisms since superconductivity is mainly enhanced near the surface [21]. This can be expressed in terms of the so called penetration depth. The problems in measuring the penetration depth arise from a property of the shielding volume fraction, namely that a thin layer of superconducting material that covers non-superconducting material results in a larger shielding volume fraction than the fraction of the sample that is actually superconducting [21, 23]. To avoid these difficulties the sample will be divided into three equal parts. The middle part will then have two surfaces opposite to each other that are not covered by a superconducting region. The penetration depth can then be determined by measuring the magnetic properties as a function of the position on the surface. By also measuring which molecules are stuck at the very surface, it can be determined which molecules and atoms penetrate the crystal and give rise to the penetration depth. Therefore it can be determined how large the effect of these molecules and atoms is, and this knowledge can also be used to determine the effect of the molecules at the surface.

There is another difficulty that arises when measurements like these have to be done on the samples. Since air exposure is known to influence the shielding volume fraction in the sample [21], the samples cannot be stored in air. Storing the samples in vacuum is difficult due to technical challenges, but more importantly it does not fully prevent exposure to air, since perfect vacuum is unachievable. This results in measurable effects on the shielding volume fraction [21]. Therefore it is necessary to store the sample in an inert atmosphere. The common choices for inert atmospheres are nitrogen and argon. Nitrogen would, however, cloud the measurements of the molecules that are involved, since nitrogen atoms might play a role in the process. Therefore argon is chosen as the inert atmosphere to store the samples in. During the research it will be explicitly checked that argon does not influence the shielding volume fraction, which is to be expected, since argon is a noble gas. To prevent other gases that might be inside the crystal to leave the crystal while it is stored, the samples will be stored in argon gas under pressure.

## 6.4 Measurement methods

In this section the preferred measurement methods for this research project will be briefly explained together with the reasons as to why they are fit for obtaining the desired information.

### 6.4.1 Mass spectrometry

Mass spectrometry (MS) is a technique which is used to find which atoms and/or groups of atoms are present within a sample. This technique first ionises the molecules in the sample and then determines the mass over charge ratio of the ions. The ionisation methods used in this research project will be laser assisted inductively coupled plasma (LA-ICP) and matrix assisted laser desorption ionisation (MALDI). The LA-ICP ionisation will be used for the MS of the crystals because other methods are not strong enough to ionise ceramic samples. MALDI will be used for the MS on the media used in the reverse annealing, this is because this form of ionisation is suitable for wine samples and therefore also for solutions containing substances out of wine [24]. Not only for the ionisation are different techniques but also for the measuring of the mass over charge ratio of the ions.

For this research two different methods seem suitable, Fourier transform (FT) MS and time of flight (TOF) MS. FT-MS is a very precise technique which seems fit for the MS of the crystal itself because it is likely that the concentrations of foreign substances in the sample is very small. The reason for this high precision is that the data of a Fourier technique like FT-MS are accumulative which means that simply measuring more cycles will yield a higher signal to noise ratio. Also measuring longer will yield a higher resolution. For the media used in the reverse annealing TOF will be used because this is suitable for wine in combination with the MALDI [24].

Mass spectrometry is an excellent way to analyse the chemical composition of a material quantitatively. This is the reason it would be very fit for analysing the contents of the sample after reverse annealing. Mass spectrometry usually gives more information than methods like an electron probe micro-analyzer (EPMA) because with mass spectrometry bigger fractions than only the elements themselves are measured which means that there is also information about the kind of molecules that were present rather than only the elements. For the identification of the analysed substances a reference database can be used. The big disadvantage of MS is that the method is destructive which means that this technique can only be applied to samples that have had their full treatment, this is why between steps non destructive techniques are used like EPMA even though they provide less information.

#### **6.4.2 Magnetometer**

A magnetometer is a device used to measure magnetic fields. This is often used to determine the magnetic susceptibility of a material, but also to measure the shielding volume fraction of a type two superconductor [23]. For the latter usually a superconducting quantum interface device (SQUID) magnetometer is used. To determine the shielding volume fraction, a magnetic field is applied to the sample and the SQUID magnetometer then measures the field strength present on the opposite other side of the sample. A type two superconductor has both superconducting and non superconducting regions and those superconducting regions will expel the applied magnetic field while the other regions will let it pass through [25]. The fraction of the magnetic field that passes through the sample is measured and that is used to calculate the fraction that is shielded, which is the shielding volume fraction. This method is useful for this research because the shielding volume fraction is the parameter used to determine the improvement in superconductivity.

#### **6.4.3 Magnetic force microscopy**

Magnetic force microscopy (MFM) is a variation on atomic force microscopy (AFM). In MFM the tip of the microscope is magnetic and therefore the magnetic properties of a material as function of the position can be determined. MFM uses a sharp tip that scans the surface and records the forces exerted on the tip. Because MFM uses a magnetic tip, superconducting regions will exert a force on the tip to expel the magnetic field created by the tip. Therefore this technique can be used to map the superconducting regions. This is especially useful when determining the penetration depth of the reaction because this method can very precisely determine the areas which are superconducting when the crystal is cut.

#### 6.4.4 Nuclear Magnetic Resonance

Nuclear magnetic resonance (NMR) is a widely used analysis technique in organic and inorganic chemistry. It uses the spin of the nuclei in a sample to gain information about their electronic environment. This information can then be used to identify molecules. NMR is in all modern spectrometers a Fourier technique which means that the signal to noise ratio can be improved by accumulating the data of multiple measurements. NMR is quite specific because different types of nuclei can be measured separately, for example only proton or only carbon nuclei. This specificity makes the technique very effective in identifying different compounds as the data from different types of nuclei can be compared.

NMR can also be used in combination with chromatography for fingerprinting of complex mixtures [26]. Using the data from this fingerprinting together with mass spectrometry data makes these techniques very powerful in identifying substances by comparing their spectra to a database. This makes it fit for identifying the substances present in the media used for reverse annealing.

#### 6.4.5 X-ray photoelectron spectroscopy

X-ray photo-electron spectroscopy (XPS) is a spectroscopy method used to identify the composition of the surface of a sample [27]. This technique uses monochromatic x-rays to ionise atoms in the surface of a sample. The electrons in the sample can absorb the energy of the photon and those exited electrons use some of that energy to overcome the ionisation energy. The rest of the photonenergy is converted to kinetic energy of the electron [27]. The kinetic energy of those electrons is then measured using an electrostatic analyser and because the ionisation and photon energies for different elements are known, the composition of the surface of the sample can be determined. The penetration depth of XPS is between 0.5 and 5 nm [28]. This technique is very valuable for this research in combination with an electron probe micro-analyzer (EPMA) because the combination of these methods could be used to distinguish the bulk and surface compositions in a non destructive way. This should give an indication as to which atoms or molecules could be responsible for the change in shielding volume fraction. This is especially useful in combination with magnetic force microscopy which tells what parts of the crystal are superconducting.

#### 6.4.6 Gas Chromatography

Gas chromatography (GC) is a separation method where the setup consists of two parts, a column (stationary phase) and a moving carrier or eluent with the sample (mobile phase) [29]. The method that is most often used is adsorption chromatography which means that the surface of the column interacts with the mobile phase, this interaction slows down molecules that have a stronger interaction with the column than the other molecules in the mobile phase. The stronger the interaction, the more those molecules are slowed and the longer they take to get through the column. The time needed to pass through the column is the retention time, this time is specific for the type of molecule and the type of column. Gas chromatography is often used in combination with mass spectrometry (MS) to do a GC-MS experiment. This way the compounds are first separated with GC and then the separate compounds are analysed with MS to identify them. The same principle is used to combine NMR with chromatography.

#### **6.4.7 X-ray diffraction**

X-ray diffraction is the standard way of determining the structure of a crystal. This is done by shining monochromatic x-rays at the crystal which then diffract off a plane in that crystals depending on its orientation. This yields a diffraction pattern that shows the crystal lattice in reciprocal space. From the diffraction pattern, the lengths of the lattice vectors in real space can be determined as well as globally the electron density distribution in a unit cell [27]. Because these lattice parameters can be determined very accurately, changes in crystal structure can be detected and one can find if a certain crystal has the expected structure. This technique can also be used to find impurities in the crystal, because those impurities will have a different reflection angle at which the x-rays will be reflected. When using powder diffraction these different reflections can be detected as well as their relative intensities which forms a reasonable quantitative indication for the present impurities.

#### **6.4.8 Raman spectroscopy**

Raman spectroscopy is a technique which is aimed at detecting changes in molecular states. This can mean changes in vibrational modes, like phonons, or rotational modes. This makes it a very powerful tool to detect small changes in a sample like a change in crystal structure because this would change its vibrational or rotational modes. The technique measures the wavelength of inelastically scattered photons from monochromatic visible light which is shined at the sample. This inelastic scattering changes their wavelength due to interactions with the energy states of the material. These wavelength differences correspond to differences in energy levels of for example rotational states. This provides a fingerprint of the sample which makes it possible to recognise changes when the fingerprint of a certain substance is known. This technique is also used on superconductors since it is very sensitive to the phonons present in a certain material as well as impurities [30]. For this reason it is also very useful for this research because it can detect changes in the phonon structure and therefore in the crystal structure when there is no change in crystal structure visible with x-ray diffraction.

#### **6.4.9 Electron probe micro-analyzer**

An electron probe micro-analyzer (EPMA) is a non-destructive tool to determine the chemical composition of solids. EPMA is based on the principle that if a solid is bombarded by an electron beam, the particles of the solid will emit X-ray photons and because the wavelength of the photons are unique for each particle based on the ionization energy, the composition of the solid can be found. EPMA can be used to measure concentrations of excess iron [31] intercalated in the crystal. Furthermore EPMA can determine the Te:Se ratio in the bulk material, so it can verify the Te:Se ratio when producing the crystal and after the experiment it can be used to check if the Te:Se ratio has changed and if there are other substances that are intercalated in the crystal during the experiment. Therefore EPMA is very suitable for this research.



## 6.5 Materials

For the experiment it is expected that over 30 samples will be prepared. Among these samples are polycrystalline and monocrystalline samples. An addition of some polycrystalline samples might be required to determine the necessary amount of red wine.

**Preparation of the monocrystalline samples** The flux method can be used to create monocrystalline samples by the use of a solvent (referred to as flux). All of the compounds required to prepare a crystal will be put in a crucible and then the flux is put on top of the compounds. Now the crucible will be heated and because of that, the compounds will dissolve in the flux. The crucible will be heated to a temperature below the temperature where the compounds will decompose, so the compounds dissolve without decomposing them [32]. Now the crucible will be cooled slowly which creates a supersaturation in the crucible. This means that there is more dissolved material from the compounds than the solvent could dissolve [33] and here the crystal will be formed. A self-flux preparation method is the flux method using a flux identical to the composition of the required crystal [34].

The self-flux method will be used to synthesise monocrystalline samples of  $\text{FeTe}_{0.9}\text{Se}_{0.1}$  as described in [21]. High purity grains of iron, tellurium and selenium, with a nominal composition of  $\text{FeTe}_{0.9}\text{Se}_{0.1}$ , which is the same ratio as used in the work by Deguchi [12], will be put in an evacuated quartz tube before being sealed. This quartz tube will be sealed into another evacuated quartz tube and heated, typically at  $1070^\circ\text{C}$  for 36 hours before being cooled slowly, at a rate of around  $6^\circ\text{C}/\text{h}$ . Afterwards the mixture is ground and pelletized. The sample now again needs to be sealed in an evacuated quartz tube and heated, typically at  $650^\circ\text{C}$  for 10 hours [21].

**Preparation of the polycrystalline samples** With a solid-state reaction, polycrystalline samples can be prepared without the use of a solvent. All of the required compounds to prepare the crystal will be put in a crucible. Now the crucible will be heated, which causes that the compounds starts to react and because of that the crystal will form [35].

The polycrystalline samples of  $\text{FeTe}_{0.9}\text{Se}_{0.1}$  will be synthesised using a solid-state reaction as described in [12]. High purity powders of iron and grains of tellurium and selenium, with a nominal composition of  $\text{FeTe}_{0.9}\text{Se}_{0.1}$ , which is equally to the composition which Deguchi used in his paper [12], will be sealed in an evacuated quartz tube which is evacuated by a rotary pump. The quartz tube will be heated, at around  $650^\circ\text{C}$  for 10 hours before the sample is thoroughly ground and pelletized. The sample now again needs to be sealed in an evacuated quartz tube and heated, typically at  $650^\circ\text{C}$  for 10 hours [12].

## 7 Timetable and Funding

The research consists of multiple parts. First there will be a theoretical part in which some time will be invested to get familiarised with the current developments of the field during the research and to adjust the research methods along the way if it seems necessary. Also a literature study will be required to set up a theoretical background. This theoretical part will take 6 months. For the second part, there will be 6 months required to learn how to prepare and cut the samples and to get familiar with the measurement methods.

Afterwards there will be a practical part for 12 months. In this period the experiments as described in the outline (section 6.1) will be performed, including the preparation of the samples, the submerge in wine, the reverse annealing and cutting of the samples, all of the measurements and the data collection. The next part will contain the analysis of the data, drawing conclusions, the writing of papers and a PhD thesis. This part will take 24 months and because of this the total time-span of this research will be 4 years.

For this research project a budget to fund a PhD student for four years and to cover the travelling expenses of this student is requested. In addition to that a budget of €5000,00 is requested for consumables and furthermore a budget of €10000,00 for the use of equipment is requested.

## 8 Relevance

The results of this research will give more insights in how superconductivity works and how superconductors with more efficiency can be synthesised. In particular efficient iron chalcogenide<sup>2</sup> superconductors could be established by adapting the crystal according to the conclusions made by this research. Additional research might be necessary to confirm if the substances of red wine that enhance superconductivity in  $\text{FeTe}_{0.9}\text{Se}_{0.1}$  would also enhance superconductivity in iron pnictide or other (iron-based) superconductors.

Besides the improved efficiency, also insights in the fundamental concept of type two superconductivity could be found. When the substances of red wine with positive influence on the superconductivity have been found, analysis of what the effects of those substances on the crystal are could provide information about the conditions necessary to have efficient superconductivity, which in term could increase superconductivity in all kinds of superconductors.

This research will mostly be used by physicists working in the field of condensed matter physics because that is where the fundamental principles behind type two superconductivity to which this research contributes. Also companies using high-temperature superconductors can benefit from the results of this research since it will probably shed more light on ways to improve these superconductors. To communicate the results in this research it will be published in an appropriate journal.

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<sup>2</sup>Element from group 16 of the periodic table

## 9 Knowledge Utilisation

This research is not very likely to have an immediate influence on the general public. In the future however it will probably become very relevant as it helps in understanding the fundamental principles behind type two superconductors. Therefore it is likely to contribute to help using superconductors in a broader sense than possible today. That would also make the use of superconductors easier which in its own would change the way electronics are functioning, e.g. broad use of magnetic levitation for transport or electricity cables without power losses. The ultimate goal is of course creating a room temperature superconductor, but this will not be accomplished by this research alone. However we think that this research will contribute to more knowledge about high temperature superconductors and with that help to find a room temperature superconductor eventually. We also feel that the knowledge from this research should not only be shared with other researchers but also with the general public to show what research is being done on the subject. Also considering the amount of media exposure the papers by Deguchi et al. [7, 11, 12] got, we think that making the article openly accessible could greatly contribute to public engagement in this field of research.

## 10 Statements by the applicants

YES/NO By submitting this document we declare that we satisfy the nationally and internationally accepted standards for scientific conduct as stated in the Netherlands Code of Conduct for Scientific Practice 2012 (Association of Universities in the Netherlands (VSNU)).

YES/NO We have completed this form truthfully.

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## 12 References

- [1] Yoichi Kamihara et al. Iron-Based Layered Superconductor  $\text{La}[\text{O}_{1-x}\text{F}_x]\text{FeAs}$  ( $x = 0.05$  through  $0.12$ ) with  $T_c = 26$  K. *J. Am. Chem. Soc.*, 130(11):3296–3297, 2008.
- [2] H. Miao et al. Isotropic superconducting gaps with enhanced pairing on electron Fermi surfaces in  $\text{FeTe}_{0.55}\text{Se}_{0.45}$ . *Phys. Rev. B*, 78(13):134512, 2008.
- [3] A. Charnukha et al. Weak-coupling superconductivity in a strongly correlated iron pnictide. *Sci Rep.*, 6(18620), 2016.
- [4] Wing Chi Yu et al. Strong Coupling Superconductivity in the Vicinity of the Structural Quantum Critical Point in  $(\text{Ca}_x\text{Sr}_{1-x})_3\text{Rh}_4\text{Sn}_{13}$ . *Phys. Rev. Lett.*, 115(20):207003, 2015.
- [5] Yoshikazu Mizuguchi et al. Superconductivity in S-substituted FeTe. *Appl. Phys. Lett.*, 94:012503, 2009.
- [6] B. C. Sales et al. Bulk superconductivity at 14 K in single crystals of  $\text{Fe}_{1+y}\text{Te}_x\text{Se}_{1-x}$ . *Phys. Rev. B*, 9(094521):094521, 2009.
- [7] Keita Deguchi et al. Clarification as to why alcoholic beverages have the ability to induce superconductivity in  $\text{Fe}_{1+d}\text{Te}_{1-x}\text{S}_x$ . *Supercond. Sci. Technol.*, 25(8):084025, 2012.
- [8] Dirk van Delft and Peter Kes. The discovery of superconductivity. *Phys. Today*, 63:38–43, 2010.
- [9] Peter D. Johnson et al. *Iron Based Superconductivity*, volume 211 of *Springer Series in Materials Science*. Springer, 2015.
- [10] Y. Mizuguchi et al. Evolution of superconductivity by oxygen annealing in  $\text{FeTe}_{0.8}\text{S}_{0.2}$ . *Europhysics Letters (EPL)*, 90(5):57002, 2010.
- [11] K. Deguchi et al. Alcoholic beverages induce superconductivity in  $\text{FeTe}_{1-x}\text{S}_x$ . *Supercond. Sci. Technol.*, 24(5):055008, 2011.
- [12] K. Deguchi et al. Superconductivity in  $\text{Fe}_{1+d}\text{Te}_{0.9}\text{Se}_{0.1}$  Induced by Deintercalation of Excess Fe Using Alcoholic Beverage Treatment. *Journal of Superconductivity and Novel Magnetism*, 27(2):305–308, 2014.
- [13] W. Meissner and R. Ochsenfeld. Ein neuer Effekt bei Eintritt der Supraleitfähigkeit. *Naturwissenschaften*, 21(44):787–788, 1933.
- [14] Keita Deguchi et al. Tartaric acid in red wine as one of the key factors to induce superconductivity in  $\text{FeTe}_{0.8}\text{S}_{0.2}$ . *Physica C: Superconductivity*, 487:16–18, 2013.
- [15] Yasuna Kawasaki et al. Phase diagram and oxygen annealing effect of  $\text{FeTe}_{1-x}\text{Se}_x$  iron-based superconductor. *Solid State Commun.*, 152(13):1135–1138, 2012.
- [16] Yoshikazu Mizuguchi et al. Superconductivity in S-substituted FeTe. *Appl. Phys. Lett.*, 94(1):012503, 2009.
- [17] D. J. Singh Lijun Zhang and M. H. Du. Density functional study of excess Fe in  $\text{Fe}_{1+x}\text{Te}$ : Magnetism and doping. *Phys. Rev. B*, 79(1):012506, 2009.
- [18] V.P.S. Awana et al. Superconductivity and thermal properties of sulphur doped FeTe with effect of oxygen post annealing. *Physica C: Superconductivity*, 471(3–4):77–82, 2011.
- [19] Tatsuhiro Yamada et al. Effects of Pnictogen Atmosphere Annealing on  $\text{Fe}_{1+y}\text{Te}_{0.6}\text{Se}_{0.4}$ . *J. Phys. Soc. Jpn.*, 85(2):024712, 2016.
- [20] Y Sun et al. Effects of annealing, acid and alcoholic beverages on  $\text{Fe}_{1+y}\text{Te}_{0.6}\text{Se}_{0.4}$ . *Supercond. Sci. Technol.*, 26(1):015015, 2013.
- [21] Y. Sun et al. Annealing, acid, and alcoholic beverage effects on  $\text{Fe}_{1+y}\text{Te}_{0.6}\text{Se}_{0.4}$ . *Supercond. Sci. Technol.*, 26(1):015015, 2013.
- [22] Keita Deguchi et al. Physics and chemistry review of layered chalcogenide superconductors. *Sci. Technol. Adv. Mater.*, 13(5):054303, 2012.

- [23] Yoichi Tanabe, Tadashi Adachi, Takashi Noji, and Yoji Koike. Superconducting volume fraction in overdoped regime of  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ : Implication for phase separation from magnetic-susceptibility measurement. *Journal of the Physical Society of Japan*, 74(11):2893–2896, 2005.
- [24] Riccardo Flamini. Mass spectrometry in grape and wine chemistry. part i: Polyphenols. *Mass Spectrometry Reviews*, 22(4):218–250, 2003.
- [25] Michael Tinkham. *Introduction to Superconductivity*. Dover Publications, 2004.
- [26] Arjen Lommen, Joop M Weseman, Geo O Smith, and Hub PJM Noteborn. On the detection of environmental effects on complex matrices combining off-line liquid chromatography and 1h-nmr. *Biodegradation*, 9(6):513–525, 1998.
- [27] Peter Atkins and Julio de Paula. *Atkins' Physical Chemistry*. Oxford University Press, 8 edition, 2006.
- [28] WA Fraser, JV Florio, WN Delgass, and WD Robertson. Surface sensitivity and angular dependence of x-ray photoelectron spectra. *Surface Science*, 36(2):661–674, 1973.
- [29] Daniel C. Harris. *Exploring chemical analysis*. W.H. Freeman and Company, 5 edition, 2013.
- [30] H. Rosen et al. Raman study of lattice modes in the high-critical-temperature superconductor Y–Ba–Cu–O. *Phys. Rev. B*, 36(1):726–728, Jul 1987.
- [31] Yuta Koshika et al. Effects of Annealing under Tellurium Vapor for  $\text{Fe}_{1.03}\text{Te}_{0.8}\text{Se}_{0.2}$  Single Crystals. *J. Phys. Soc. Jpn.*, 82(2):023703, 2013.
- [32] G. Dhanaraj et al., editors. *Springer Handbook of Crystal Growth*. Springer, 2010.
- [33] Gerard Coquerel. Crystallization of molecular systems from solution: phase diagrams, supersaturation and other basic concepts. *Chem. Soc. Rev.*, 43(7):2286–2300, 2014.
- [34] Peter Rudolph, editor. *Handbook of Crystal Growth: Bulk Crystal Growth*, volume 2A. Elsevier, 2014.
- [35] Anthony R. West. *Solid State Chemistry and Its Applications*. John Wiley & Sons, 1987.