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INVESTIGATION OF KRYPTON BUBBLES IN COPPER USING X-RAY TECHNIQUES

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Master of Science

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31 May 2002
Declaration

I, the undersigned, hereby declare that the work contained in this thesis is my own original work and has not previously in its entirety or part been submitted at any university for a degree.

Date
31 May 2002

Signature

[Signature]
ABSTRACT

Investigation of the micro-mechanical properties of bulk copper, containing a high concentration (3 atomic %) of krypton is performed by X-ray diffraction techniques. Stress determination and phase analysis are carried out to determine the residual stress of the host copper metal and the internal pressure of the krypton bubbles. Lattice parameter determination of krypton bubbles confirms solidification of krypton with a fcc structure epitaxial to the host metal with a bubble pressure of 2.6 GPa. The \( \sin^2 \psi \) technique of stress determination indicates no macro residual stress inside the copper matrix as predicted by the continuum ansatz of the elasticity theory. The pressure of the krypton bubbles manifests itself as a shear strain in the copper matrix and the shear strain is found to be below the yield strength of the copper matrix, thus explaining the long-term stability.
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1 INTRODUCTION

This thesis concerns the investigation of mechanical properties of a very special, uniquely produced material, krypton-doped copper. The copper sample contains a high amount of krypton implanted throughout the whole material by a novel implantation and sputtering process. The microstructure of the copper-krypton matrix is very unusual from a material scientist's point of view, thus an overview of the historical development of the material gives a better insight of the material under investigation.

In the early 1980s, when nuclear power plants were broadly used, questions arose how to store the radioactive $^{85}$Kr isotope produced as fission product in nuclear fuel. Kr, being an inert gas, doesn't form stable bulk compounds, which are the preferred forms for storage or disposal [1]. Along with a number of possible approaches to the management of $^{85}$Kr, the idea of immobilization of krypton in a metallic matrix was considered. The metallic trapping of krypton promised several advantages over the other possible solutions (such as retention as a gas at high pressure in cylinders, which is not very convenient for obvious security reasons).

D. S. Whitmell et al. [2, 3] developed an efficient, feasible and economic process of immobilization of krypton in a metal at AERE Harwell and at Battelle Pacific Northwest. Not only copper, but a range of different materials, i.e. nickel, iron, aluminium and monel composition can be used to deposit about 170 litres of gas (at standard temperature and pressure) per litre of metal. The gas forms bubbles, typically 20 Å size, inside the matrix, so dangerous amounts of radioactive gas will not be released to the atmosphere in case of a crack or similar mechanical incident.

Little was known, at that time, about the static and dynamic properties of the trapped atoms and the elastic response of the copper matrix. The production of the krypton containing Cu, Cu(Kr), ignited a broad study of gas bubbles in metals. An overview of the sample properties, by describing the past studies and their results is given in the
next chapter. Transmission Electron Microscopy (TEM) and Small Angle Neutron Scattering (SANS) measurements and other methods were applied to understand the micro-mechanical state of the sample. On the other hand, the question of stability of the krypton atoms inside the copper matrix should be answered by the theory of elasticity. The residual stress inside the copper must be evaluated and it must be confirmed that the metal is capable of holding the bubbles inside for an extended period of time.

The macro and micro residual stresses (see Chapter 3.2) play a critical role in the strength of any material's mechanical behaviour. In this work, X-ray diffraction has been used to evaluate the macro residual stress and compare it with the maximum stress the copper can sustain safely. The present study includes the calculation of pressure inside the bubbles and the macro residual stress in the matrix. First the continuum ansatz of elasticity theory will be developed after Mott & Nabarro [4] and the experimental results are compared with the predictions of the theory.

Although the original material was produced to solve practical problems of nuclear waste disposal, the Cu(Kr) sample offers the opportunity of studying noble gas solids at room temperature (RT) [5]. This is an invaluable possibility to learn more about the thermodynamics of solidification. The investigation of mechanical properties can open up new areas of application both in science and technology.
2 SAMPLE CHARACTERISATION AND HISTORY

The sample under investigation is a bulk material composed of two extremely different elements. The host material (copper) is a widely used metal and the guest element is an inert gas (krypton). The properties of these elements are summarised in Table 2.1. The synergy of combining these two extremely diverse materials has very far-reaching properties but it is essential to have an overview of the both elements before further investigation of the Cu(Kr) product.

Copper is a brownish-red metallic element that is has many application fields and has been known to human beings from very early history. It is a solid under standard temperature and pressure (STP: 1 atm, 0°C). Its value is mainly due to its high conductivity, malleability, resistance to corrosion and beauty. Copper is also very ductile, that is forced deformation can occur without breaking or splintering. Ductility plays a crucial role in a material’s fracture toughness. Ductile materials have a strong resistance to breaking when a crack is present.

The tensile strength of pure copper is about 340 MPa [6]; it can be used in outdoor power lines and cables, generators, motors and communication equipment. Pure copper can be hardened by being worked on. Alloys of copper are far harder and stronger than the pure metal.

<table>
<thead>
<tr>
<th></th>
<th>COPPER</th>
<th>KRYPTON</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Atomic weight</strong></td>
<td>63.55</td>
<td>83.39</td>
</tr>
<tr>
<td><strong>Atomic size</strong></td>
<td>1.45 Å</td>
<td>0.88 Å</td>
</tr>
<tr>
<td><strong>Melting Point (1 atm)</strong></td>
<td>1356 K</td>
<td>115.79 K</td>
</tr>
<tr>
<td><strong>Boiling Point (1 atm)</strong></td>
<td>2840 K</td>
<td>119.65 K</td>
</tr>
<tr>
<td><strong>Density</strong></td>
<td>8960 kg/m³</td>
<td>-</td>
</tr>
<tr>
<td><strong>Crystalline structure</strong></td>
<td>FCC</td>
<td>FCC</td>
</tr>
</tbody>
</table>

Table 2.1 Properties of copper and krypton elements
On the other hand krypton is a colourless, odourless inert gas at STP. It makes up a tiny fraction of the earth’s atmosphere (1:20 million) [7. Krypton, being an inert gas, does not react chemically with other elements.

The density of krypton in the gas state is not defined in Table 2.1, simply because the densities of gases change in a large range from $10^{-5}$ to $10^1$ g/cm$^3$ depending on the temperature and the pressure. Atomic size calculations are carried out by the method explained in [8]. The atomic size of krypton is smaller than copper though krypton has more electrons orbiting due to its larger atomic number (Figure 2.1). Krypton is at the bottom of the third period and copper is roughly in the middle. Solid krypton melts at 115 K and evaporates shortly after at 119.65 K at atmospheric pressure. Liquefaction and even more importantly solidification of krypton at room temperature, therefore, requires very high pressures.

![Atomic size comparison](image.jpg)

**Figure 2.1 Relative atomic sizes of elements** [9]

Combining a famous ductile metal with an inert gas leads to the alteration of physical properties of the host material. The mechanical properties of the new bulk material are especially interesting in the sense that the metal-inert gas system comprises a stable bulk material. Because the krypton atoms will not react with the surrounding copper atoms and being insoluble they will tend to form precipitates inside the metal matrix [10]. But the very process of incorporating krypton atoms inside the metal matrix requires special techniques.
Two different production techniques can be implemented for the incorporation of krypton inside the copper metal:

1. ion implantation
2. combined implantation/sputtering

2.1 **ION IMPLANTATION**

Ion implantation is a well-known alloying technique which has been used in many different applications [11]. Beams of ions of carbon, nitrogen and other elements are fired into selected metals in a vacuum chamber to produce a strong, thin modified region at the surface [12]. The ions enter the material with high velocity and dissipate their energy through a series of collisions. In the process they travel a distance R, called the range, which is larger than then the perpendicular distance penetrated below the surface of the material before coming to rest. The implantation process directly affects to the near surface region of the host material, nevertheless the physical properties of the whole material could be altered spectacularly. Bombarding titanium with nitrogen, for example, can produce a superior alloy for prosthetic implants [13].

2.2 **COMBINED IMPLANTATION & SPUTTERING PROCESS**

The combined implantation/sputtering process [1] is capable of producing a homogeneous impurity distribution throughout the host metal (copper in our case). With the conventional implantation process, end products would have only guest ions near the surface of the sample.

The equipment used for combined sputtering/implantation, consists of two main parts, Figure 2.2. A copper cylinder is placed inside the centre of the vessel and a second thin metallic cylinder with a larger radius is placed coaxially with the first one. Krypton gas is inserted in the space between two coaxial cylinders with a typical
pressure of 10 kPa. A glow discharge generates ions by applying a voltage of 3-5 kV between coaxial cylinders.

Figure 2.2 Schematic diagram of the AEERE Harwell Vessel [1]

A procedure capable of producing bulk material with impurity atoms was introduced by Whitmell [1]. The principles of the implantation/sputtering process are shown in the Figure 2.3.

This discharge is the source of ions used for both implantation of krypton atoms and sputtering of the centre electrode. The krypton gas atoms are implanted into the outer electrode by switching the negative voltage to this electrode (see Figure 2.3a). The implanted layer is then coated with a layer of material sputtered from the inner electrode by switching the voltage to the inner electrode; see Figure 2.3b. By repeating the process, typically a few times a second, a thick layer of bulk material is built up. The process is controlled by adjusting the voltages and the electrical controls.
Figure 2.3 *Principle of the Harwell combined implantation and sputtering process.*

*After Whitmell [1].*

(a) *Implantation of inert gas atoms*

(b) *Sputtering of metal layers so that gas bubbles form in a metal matrix*

Some physical properties of the Cu(Kr) product of the Harwell process had been previously measured shortly after production [1]. The thermal conductivity is 80 Wm⁻¹K⁻¹. It is very hard, with a Vickers hardness number of 340. The specific heat and melting points are similar to many copper alloys [1]. The bulk density is slightly (5%) lower than pure copper, 8.46 g/cm³ [14] compared with 8.92.

### 2.3 SAMPLE CHARACTERISATION

A 10 x 10 x1 mm³ sample was cut from the bulk material produced by the previously described process. The normal of the sample surface is perpendicular to the growth direction as seen in Figure 2.4.
The material from which the sample, under investigation here, was cut has been investigated using a variety of methods and plenty of information about it is available [1, 15-17]. Firstly, transmission electron microscopy (TEM) was used by Evans et al. to study the structure of the sample [15]. The TEM micrograph of the Cu(Kr) material clearly shows the high density of small krypton bubbles inside copper (Figure 2.5). The krypton atoms are trapped in spherical bubbles in a polycrystalline matrix with very small (0.2-0.3 μm) randomly orientated grains. The bubbles have diameters of 15-20 Å and are randomly arranged with a density of \(4 \times 10^{24} \text{ m}^{-3}\) [14], i.e. the average distance is about 40 Å. When the deposit is heated bubbles in the grain boundaries grow and eventually interlink and intersect the surface [1].

Electron diffraction studies with Cu(Kr) sample was carried out by Evans and Mazey in 1985 [16] and are generally in agreement with TEM measurements. The electron diffraction pattern of an (011) Cu(Kr) is shown in Figure 2.6. The krypton was confirmed to be solid, for the first time, with an FCC structure.
Figure 2.5 *TEM micrograph of krypton bubbles in copper.* Krypton bubbles can be seen as tiny dots on the left picture (b) [14].

The weaker small spots next to the bright copper diffraction spots are from the crystalline krypton. The lattice parameter was estimated to be 5.2 Å corresponding to an atomic density of $2.85 \times 10^{28} \text{ m}^{-3}$.

![Figure 2.5](image)

Figure 2.6 *Electron diffraction pattern of the bulk Cu(Kr) material.* Krypton peaks are very weak in intensity compared to copper peaks. This is due to small amount of krypton content in the bulk material [16].
Further studies revealed other properties of the sample. Average krypton content is estimated to be 3.3 at % [1]. Small angle neutron scattering measurements (SANS) performed by Pedersen et al. [17] on the same material, estimated that ½ of the krypton is confined in the bubbles of a size exceeding 15-20 Å in diameter.

The solidification of krypton at room temperature is an indication of high-pressure values inside the copper matrix.
3 THEORETICAL BACKGROUND

3.1 INTRODUCTION

The internal forces inside the materials are what keep them solid. Solid materials do have resistance to all applied external forces. The external forces can be divided into two categories [6]. One type of these force couples tries to compress or stretch the material, while the other type tries to twist or bend the material. These forces introduce compressive or tensile stress and shear stress, respectively inside solids. Fluids do sustain compressive stresses, but under applied shear stresses fluids simply flow. Only solids can support shear stresses.

Materials subject to external forces deform. The mechanics of the deformation all depend on the microstructure of the material. The interatomic or intermolecular forces try to compensate the applied external forces in order to get the material in an equilibrium state. The material will either go to a stable equilibrium state with stress fields built inside itself or break.

Stress and strain are two quantities used to quantify a state of deformations. Stress is defined to be the force per unit cross sectional area. Shear stress is a tangential force per unit area that tends to shear a body. The extension/contraction per unit length is called the strain. It has been experimentally confirmed that for a large number of materials strain is linearly related to the stress (Hooke's law) see, e.g. [19], for the initial range of loading.

After releasing the applied forces from a solid, the solid will relaxes and the general structure of the solid will re-arrange to minimize the internal energy stored in the chemical bonds of the material. If the solid returns to its original size and shape after the deformation is removed, the deformation is said to be elastic, otherwise the material is said to be inelastically deformed. Inelastic deformations always end up with residual stresses inside the material, see e.g. [20].
3.2 Residual Stress

Residual stress is the stress inside a material without any applied forces. It is easy to see residual stress of solids around us. A straight, say copper, wire after being cut into two pieces will often bend because of the residual forces, which were balanced before cutting the material. Cutting introduces two surfaces and the internal forces (residual stresses) reform the wire to take a curved form (Figure 3.1).

![Figure 3.1 Observing residual stresses by cutting of a copper wire](image)

Residual stress can be exploited to design materials or components, which are resistant to damage, toughened glass being a good example [21].

Macro residual stresses extend over a long range relative to the scale of the specimen's microstructure [20]. These stresses originate from differential plastic flow, differential cooling rates (thermal stresses), or phase transformations with volume changes. Welding, forging, casting, rolling, machining, surface treatments, or heat-treating creates macro residual stresses. For example, the breaking of a cool tea glass upon pouring hot tea in, is an everyday example of thermal stresses. These stresses are often high at the surface of a material or at specific locations within the specimen. Their variation across a surface or through thickness can be critical to material performance (see e.g.[21]).

Micro residual stresses originate from a number of different ways. The differential thermal expansion between phases or differential plastic flow between grains is a typical example [21]. For example, micro stresses that develop in composites primarily result from differences in the respective thermal expansion coefficients.
Micro residual stresses also form inside material if there is a dislocation or point defect inside the material (see e.g. [22] and Figure 3.3).

Figure 3.2 Structure of an edge dislocation. The matrix is under tension in the lower part and there is compressive stress in the upper part. From Kittel [22]

Figure 3.3 Lattice distortions due to point defects. From [23]
(a) Vacancy
(b) Interstitial atom

In this work, we are interested in residual stresses originating from impurities inside the crystal structure of the bulk material. In particular, the very process of implanting krypton introduces residual stress by manipulating the microstructure of the material.
The implantation process is described in detail in the previous chapter. The implanted krypton 'bubbles' are under pressure from the surrounding copper atoms and the copper atoms also suffer stress to keep the krypton atoms inside the matrix. In the following the mathematical models used model to describe stress, strain and thermodynamics of the bubbles are presented.

3.3 ELASTICITY AND THE CONTINUUM THEORY

The theory of elasticity describes the condition of stress and strain inside an elastic material, which is twisted and deformed in some complicated way. We will start with describing the local strain at every point in an elastic body, following the textbook of R.P. Feynman [19].

We start with the material initially unstrained and watch a certain point P on / in the material when the strain is applied. Say, point P from \( r = (x, y, z) \) moves to a new point \( P' = (x', y', z') \) as shown in Figure 3.4. Let us define the vector displacement vector \( u \) from P to P'.

\[
u = r' - r
\]

\( u \) is the local displacement and is a function of position. So it depends on which point P is.

Before deformation

\[ \begin{array}{c}
\text{P} \\
\text{r}
\end{array} \]

After deformation

\[ \begin{array}{c}
P' \\
\text{r'}
\end{array} \]

\[ \begin{array}{c}
\text{u}
\end{array} \]

Figure 3.4 Point P moves from P to P' during deformation. From Feynman [19]

The strain in any direction, say \( x \), will vary from place to place in the material. For the general situation we can define the \( e_x \) by a kind of local strain, namely by
\[ e_{xx} = \frac{\partial u_x}{\partial x} \] (3.2)

Similar equations will hold for \( y \) and \( z \).

To describe shear type strains we will introduce more terms to the local strain. Suppose that a cube shaped material is pushed out of shape, it may get changed to parallelepiped, as sketched in Figure 3.5. In this kind of strain, the \( x \)-motion of points is proportional to its \( y \) coordinate,

\[ u_x = \frac{\theta}{2} y \] (3.3a)

and there is also a \( y \)-motion proportional to \( x \),

\[ u_y = \frac{\theta}{2} x. \] (3.3b)

![Figure 3.5 Pure shear strain of a square sheet. From Feynman [19]](image)

(a) Before deformation  
(b) Deformed under pure shear strain

So we can describe shear type strains by writing
\[ \varepsilon_x = \varepsilon_{xy} y, \quad \varepsilon_y = \varepsilon_{yx} x \]  

(3.4)

with

\[ \varepsilon_{xy} = \varepsilon_{yx} = \frac{\theta}{2}. \]  

(3.5)

There is one problem left after defining the shear strains, the sum of \( \varepsilon_{xy} \) and \( \varepsilon_{yx} \) should be zero for pure rotations, where the whole material rotates in space (Figure 3.6). We must somehow make our definitions so that pure rotations are not included in our definitions of shear strain. The key point is that, for pure rotations \( \varepsilon_{xy} \) and \( \varepsilon_{yx} \) are equal in magnitude but opposite thus,

for pure rotation \( \varepsilon_{xy} = -\varepsilon_{yx} \)  

(3.6)

Figure 3.6 Rotation of a pure square sheet. From Feynman [19]

(a) Before rotation

(b) New orientation after rotation. There is no deformation.
The problem can be solved by defining,

$$\varepsilon_{xy} = \varepsilon_{yx} = \frac{1}{2} \left( \frac{\partial u_y}{\partial x} + \frac{\partial u_x}{\partial y} \right)$$  \hspace{1cm} (3.7)

In the most general distortion, which includes stretching, compression as well as shear, we can define the state of strain by giving the nine components of the \textit{strain tensor}.

$$\frac{1}{2} \left( \frac{\partial u_m}{\partial r_n} + \frac{\partial u_n}{\partial r_m} \right) = \varepsilon_{mn} = \begin{pmatrix} \varepsilon_{11} & \varepsilon_{12} & \varepsilon_{13} \\ \varepsilon_{21} & \varepsilon_{22} & \varepsilon_{23} \\ \varepsilon_{31} & \varepsilon_{32} & \varepsilon_{33} \end{pmatrix}$$  \hspace{1cm} (3.8)

By definition $\varepsilon_{ij} = \varepsilon_{ji}$, leaving 6 numbers to define the local strain at any point. Therefore local strain at any point of a material is a \textit{symmetric tensor} of 3rd rank.

### 3.4 Tensor of Elasticity

We have described the strains, now we must relate them to the internal forces, or the stresses inside the material. For each small piece of the material we assume that Hooke’s law holds and write that the stresses are proportional to the strains. The stress tensor is defined to be the $\sigma_{ij}$ as the $i$th component of the force across a unit area perpendicular to the $j$-axis. Hooke’s law states that each of the stress component is linearly related to each of the components of the strain tensor. Both $\sigma$ and $\varepsilon$ are symmetric tensors with 6 components; we can relate them by writing

$$\sigma_{ij} = \sum C_{ijkl} \varepsilon_{kl}$$  \hspace{1cm} (3.9)

Since the coefficients of $C_{ijkl}$ relate one tensor to another, they also form a tensor of fourth rank. We call $C_{ijkl}$ the \textit{tensor of elasticity} and the components elastic constants.
If we know the strains then we can also work out the stresses and *vice versa* by using Equation (3.9). In the general form $C_{ijkl}$ has 81 components. This number decreases to 21 because both $\sigma_{ij}$ and $\varepsilon_{kl}$ are symmetric. This holds for a triclinic crystalline system. It reduces further for crystal structures of higher symmetry. In the case of isotropic polycrystalline materials there are only two independent components [20].
4 STRESS & STRAIN AROUND SPHERICAL INCLUSIONS

4.1 INTRODUCTION

Bulk Cu(Kr) is produced as discussed before (Section 3). The bulk material contains krypton bubbles which are located inside the crystalline copper matrix. The inclusions obviously change the microstructure of the material compared to pure copper. The crystalline structure of the copper matrix is deformed by the krypton guest atoms or agglomeration of krypton atoms. Krypton bubbles, as the previous literature calls them [5, 16, 25], are formed by migration of single krypton atoms inside the copper matrix [14] to very small agglomerates, which can assumed to be spherical for further investigation. The spherical form of the bubbles has also been confirmed by TEM (see Fig 2.6) [16].

The strains in the material will be investigated by X-ray diffraction techniques. The stress of the copper matrix will be measured using strain determination. The stress and strain inside the copper are influenced by the microstructure. It is essential to understand the mechanics of stress and strain in materials to interpret the results coming from the stress diffraction measurements.

The stresses caused by inclusions are also responsible for the change of physical properties of materials, for example hardening of materials. If the mechanisms of micro structural dislocations are understood, then the degree of hardening can be predicted [4]. The mathematical theory of inclusions will help to understand hardening procedures.

4.2 CONTINUUM ANSATZ OF ELASTICITY THEORY

In this section the stress formed by spherical precipitates is described, following Mott, Nabarro [4]. We will assume that the precipitates are located in an infinite continuum. We call the inclusion the precipitate (Figure 4.1).
The *matrix* is defined as the infinite continuum made up of small volume elements. In other words, we divide the infinite continuum into small volume elements of infinitesimal size.

![Figure 4.1 2-D representation of spherical precipitate in an infinite volume.](image)

In Figure 4.1, the precipitate is assumed to be under hydrostatic pressure from the matrix. We assume further that the volume elements in the precipitate are the same size with the volume elements in the matrix. Thus the precipitate is actually experiencing no external pressure.

Let us think of a precipitate, which has a larger atomic spacing than the original matrix. Thus the volume elements of the precipitate are larger than the matrix (Figure 4.2). The matrix will not let the precipitate expand freely and the precipitate will experience pressure from the matrix outside. The precipitate will expand outwards until it is in equilibrium with the outer matrix and the pressure inside the precipitate and the pressure in the matrix outside will be equal across the interface (Figure 4.2). The expansion is spherically symmetric. A similar treatment has been presented by Schmauder [26] for thermal stresses caused by differential thermal expansion between a spherical inclusion and an elastic matrix.
The strain inside the precipitate is hydrostatic; each volume element experiences the same strain ($\varepsilon$).

Figure 4.2 Precipitate relaxes until it is in equilibrium with the matrix.

We consider a spherical inclusion of radius $r_0$ embedded in the middle of an infinite matrix. We shall assume that under zero pressure the atomic volume $V_i$ of the inclusions bears a ratio to that of the matrix $V_m$ given by

$$\frac{V_i}{V_m} = \frac{(1+\delta)^3}{1}$$  \hspace{1cm} (4.1)

If the $V_i$ is larger than $V_m$, i.e. $\delta > 0$, then the material of the inclusion will be under hydrostatic pressure. Inside the copper matrix the precipitate is under hydrostatic pressure, thus it will be smaller than its zero-pressure volume. The new ratio of volumes will be

$$\frac{V_i}{V_m} = \frac{(1+\varepsilon)^3}{1}$$  \hspace{1cm} (4.2)
where $\varepsilon < \delta$.

The relaxation ends up with an isotropic displacement inside the precipitate ($r < R_0$ where $R_0 < r_0$ is the equilibrium radius of the precipitate). In Figure 4.2, the precipitate in the centre shows this. This corresponds to larger volume elements inside the precipitate. The displacement yields a constant strain inside, i.e. linear displacement inside.

Let $u(r)$ represent the displacement of the medium at a distance $r$ from the centre of the inclusion. Elasticity theory gives us the most general form for $u(r)$ with spherical symmetry

$$u(r) = Ar + \frac{B}{r^2} \tag{4.3}$$

where $A$, $B$ are constants and $r$ is the position vector where we want to find the displacement, $u(r)$.

In our case we can write

$$u(r) = \sigma r \quad \text{when } r < R_0, \tag{4.4}$$

$$u(r) = \frac{\varepsilon R_0^3}{r^2} \quad \text{when } r > R_0. \tag{4.5}$$

We can calculate the hydrostatic pressure of the spherical precipitate by using the strain inside the sphere. Let $B$ be the Bulk modulus of the precipitate. The strain in the inclusion is a uniform hydrostatic compression $3(\delta - \varepsilon)$, and hence the pressure is given by

$$p = 3B(\delta - \varepsilon) \tag{4.6}$$

A different situation arises outside the precipitate, for the volume elements of the matrix. The matrix tries to resist the expansion of the precipitate from all directions in space. The
net effect will be that the matrix will experience a deformation too, in a degree related to the precipitate’s strain. The more the spherical inclusion applies pressure, the more the copper experiences an elastic deformation.

The deformation of the copper matrix is very interesting due to the fact that the volume elements inside the matrix do not change in volume but only in shape. Because only the shape of the volume elements changes, not the size, this indicates that only shear stress in the matrix. The net effect of the spherical precipitate inside the matrix is that they apply a shear stress on the matrix. The matrix only suffers from a shear stress, so there is no normal component of the stress inside the matrix. This reduces the stress sensor to 3 off-diagonal elements.

If we turn back to the displacement vector \( u(r) \), equation (4.3) the second term describes the behaviour in the matrix. This is given by equation (4.5).

This form of the displacement fulfils Laplace’s equation

\[
\frac{\partial^2 u}{\partial r^2} = 0. \tag{4.7}
\]

This means that \( u(r) \) is the derivative of Lamé’s strain potential [27] of the form

\[
V(\vec{r}) = C \frac{C}{\sqrt{r_1^2 + r_2^2 + r_3^2}} \tag{4.8}
\]

where \( C \) is a constant. The general strain tensor is

\[
\varepsilon_{ij} = \begin{pmatrix}
\varepsilon_{11} & \varepsilon_{12} & \varepsilon_{13} \\
\varepsilon_{21} & \varepsilon_{22} & \varepsilon_{23} \\
\varepsilon_{31} & \varepsilon_{32} & \varepsilon_{33}
\end{pmatrix} \tag{4.9}
\]
the diagonal elements are the dilatation and the off-diagonal elements are the shear components. One can conclude:

1. there is no shear strain if off-diagonal elements are zero.

2. and only shear strain if the Trace of \( \varepsilon_{ij} \) is zero.

We will now prove that trace of \( \varepsilon_{ij} \) is equal to zero with the potential \( V(r) \) given by equation (4.8) and thus the strain is pure shear.

The displacement field vector \( u(r) \) is defined as

\[
u(r) = -\nabla V(r) \quad (4.9)
\]

in components

\[
u_i(r) = \frac{C}{r^3} r_i \quad (4.10)
\]

Since we have \( u_i \), we can determine strain components easily with

\[
\varepsilon_{ii} = \frac{\partial u_i}{\partial r_i} \quad (4.11)
\]

and

\[
\varepsilon_{ij} = \frac{1}{2} \left( \frac{\partial u_i}{\partial r_j} + \frac{\partial u_j}{\partial r_i} \right) \quad (4.12)
\]
The principal (diagonal) components will be

\[ \varepsilon_{ii} = \frac{\partial \mathbf{u}_i}{\partial r_i} = \frac{C}{r^3} \left( 1 - 3 \frac{r_i^2}{r^2} \right) \]  

(4.13)

and the off-diagonal elements will be

\[ \varepsilon_{ij} = \frac{1}{2} \left( \frac{\partial \mathbf{u}_i}{\partial r_j} + \frac{\partial \mathbf{u}_j}{\partial r_i} \right) = -\frac{3}{2} \frac{C}{r^3} \frac{r_i r_j}{r^2} \]  

(4.14)

The full strain tensor is

\[ \varepsilon_{ij} = \frac{C}{r^3} \left( \begin{array}{ccc} \left( 1 - 3 \frac{r_1^2}{r^2} \right) & -\frac{3}{2} \frac{r_1 r_2}{r^2} & -\frac{3}{2} \frac{r_1 r_3}{r^2} \\ -\frac{3}{2} \frac{r_2 r_1}{r^2} & \left( 1 - 3 \frac{r_2^2}{r^2} \right) & -\frac{3}{2} \frac{r_2 r_3}{r^2} \\ -\frac{3}{2} \frac{r_3 r_1}{r^2} & -\frac{3}{2} \frac{r_3 r_2}{r^2} & \left( 1 - 3 \frac{r_3^2}{r^2} \right) \end{array} \right) \]  

(4.15)

Note that \( \varepsilon_{ij} = \varepsilon_{ji} \).

The trace of the strain tensor is

\[ \text{Tr} \varepsilon = \frac{C}{r^3} \left( 3 - 3 \frac{r_1^2 + r_2^2 + r_3^2}{r^2} \right) = \frac{3C}{r^3} \left( 1 - \frac{r^2}{r^2} \right) = 0 \]  

(4.16)

Thus the matrix experiences pure shear strain.
The shear stress in the matrix can easily be derived by introducing [4]

\[
\varepsilon = \frac{3B\delta}{3B + 2E/(1 + \nu)}.
\]  

(4.17)

where \(E\) is Young’s modulus and \(\nu\) is Poisson’s ratio of the matrix. Finally, the shear stress \(\sigma = G\,\varepsilon\) can be found by using the shear modulus

\[
G = \frac{E}{2(1 + \nu)}.
\]  

(4.18)

where \(G\) is the shear modulus of the copper matrix.

The pressure in the krypton bubbles (equation 4.6) must be equal to the radial component of the stress of the copper matrix at the matrix-bubble interface.

\[
P_{\text{bubble}} = \sigma_{\text{radial}}
\]  

(4.19)

Equating (4.6) and (4.17) we find that

\[
\sigma = G\varepsilon = \frac{P}{4}
\]  

(4.20)

Equation (4.20) relates the pressure of the krypton bubbles to the shear stress of the surrounding copper matrix at the bubble-matrix interface. The stress decreases rapidly from the centre of the bubble with an \(r^{-1}\) law.

The previous result states that the inclusion only changes the shapes of the volume elements in the matrix but not their size.
5 RESIDUAL STRESS DETERMINATION WITH X-RAY DIFFRACTION TECHNIQUES

5.1 Basic Diffraction

It has been possible to ‘see’ the inside of matter since the beginning of last century by X-ray techniques. It was the first quantitative measurements after Democritus’ atomic hypothesis, which states that all matter is composed of tiny building units (atoms) piled in different structures, and dates back to 450 BC. Before X-ray diffraction, there was little knowledge about the interior structure of matter, though it was believed that crystals were built by repetition of some base units, of size 1-2 Å (see e.g. [21]). On the other hand, X-rays are electromagnetic waves of approximately 1-2 Å wavelengths. The German physicist von Laue first reasoned that:

a) If crystals are composed of regularly spaced atoms which may act as scattering centres for X-rays,

b) and if X-rays are electromagnetic waves of wavelength about equal to the interatomic distance in crystals,

then it should be possible to diffract X-rays by means of crystals (see e.g.[21]). The diffraction experiments of von Laue proved that crystals have a periodicity of the arrangement of atoms within a crystal and diffract X-rays to result in diffraction patterns, which can, then, be used to learn more about the crystal structure of matter.

The diffraction phenomenon takes place when waves of any kind interact with matter. After the interaction, incoming waves may be scattered in all directions. In our case, the atoms of the crystals scatter X-rays in all directions. In some of these directions the
scattered beams will be completely in phase and so reinforce each other to form diffracted beams (Fig 5.1).

Consider two monochromatic X-ray beams, 1 and 2 in Figure 5.1, both at the same phase coming to the crystal with an angle of \( \Theta \). Ray 1 is reflected from the top crystal plane and ray 2 from the next plane. The path difference from A to B

\[
\Delta x = 2d \sin \Theta
\]  

(5.1)

corresponding to a difference in phase of

\[
2\pi \frac{\Delta x}{\lambda}
\]

(5.2)

\[\text{Figure 5.1 Principle of diffraction}\]

Scattered rays 1' and 2' will be completely in phase if this path difference is equal to a integer multiple, \( n \), of wavelengths (Bragg's law),

\[
n \lambda = 2d \sin \Theta.
\]  

(5.3)
The crystal lattice plane spacing $d$ can be measured accurately with a proper set-up. By knowing $d$ one can calculate the crystal lattice parameter $a$ using space geometry of lattice structures. The crystal is cubic

$$d^2 = \frac{a^2}{h^2 + k^2 + l^2}$$  \hspace{1cm} (5.4)

Combining Bragg’s Law with (5.4), we get

$$\sin^2 \Theta_{hl} = \frac{\lambda^2}{4a^2} (h^2 + k^2 + l^2)$$  \hspace{1cm} (5.5)

and similarly for the other crystal structures.

We conclude by saying that diffraction directions are determined solely by the shape and the size of the unit cell of crystals (see [21]).

Fig 5.2 shows a typical diffraction pattern. The peaks correspond to $\Theta$ angles where the constructive interference takes place. The intensity of X-rays increases giving rise to clearly observable peaks in the diffraction pattern. Different peaks correspond to different Miller indices of the crystal lattice planes.

Figure 5.2 Sample diffraction pattern showing different diffraction peaks
5.2 Effects of Strain in Diffraction Patterns

In this section, the effects of micro and macro stresses on the diffraction pattern are discussed. The term 'residual stress' refers to the internal stress after mechanical or thermal processes applied on a poly- or single crystalline material. The residual stress is somewhat more complex in polycrystalline material because the change in any grain is determined not only by the forces applied to the piece as a whole, but also by the fact that each grain retains contact on its boundary surfaces with all its neighbours [21]. Thus some grains having a special direction can suffer more strain whereas other grains facing some other direction will not strain that much.

Stresses that vary from grain to grain (or even from one part of the grain to the other part) are called microstresses. One the other hand the stresses may be uniform over large distances and are called macro stresses.

To see the effect of both kinds of strain, consider the unstrained crystal and the corresponding diffraction line shown in Figure 5.3a. If the lattice is given uniform tensile strain at right angles to the lattice planes, their spacing becomes smaller than $d_0$, and the corresponding diffraction line shifts to higher angles, but doesn’t otherwise change (Figure 5.3b). This line shift is the basis of macrostresses, because one can calculate the strain directly from the shift of the diffraction peak. If the material is bent, then the strain will not be uniform throughout the material. There will be tensile strain on the outer side and compressive strain on the inside. And the lattice spacing will be larger on the top part while it will be less in the bottom part, and at some position in between the lattice plane will not suffer any strain. We may imagine this crystallite to be composed of a number of small regions each having the same plane spacing but different from the spacing in the adjacent regions. All different regions will contribute to the diffraction pattern with different diffraction lines, dotted lines in Figure 5.3c and we will see the sum of these sharp lines.
Figure 5.3 *The effect of micro and macro residual stress on the diffraction patterns. From [21]*

(a) Unstrained material

(b) Uniform strain causes a shift on the diffraction line

(c) Non-uniform strain causes peak broadening due to a multitude of diffraction peaks generated by non-uniform strains

### 5.3 Strain Equations

In this section, the basic equations of residual stress determination with X-ray diffraction are derived. The orthogonal coordinate system used in the following discussions is shown in Figure 5.4.
The specimen coordinate system is denoted by \( S_j \) coordinates. The axes \( S_1 \) and \( S_2 \) are the axes that lie on the specimen surface. The laboratory system \( L_i \) is defined such that \( L_3 \) is in the direction of the normal of the planes \((hkl)\) whose spacing is measured by X-rays. \( L_2 \) is in the plane defined by \( S_1, S_2 \) and makes an angle \( \Phi \) with \( S_2 \).

**Figure 5.4** Definition of the laboratory and sample coordinate systems, angles \( \Phi \) and \( \Psi \) [29]

We will follow the conventions established by Dölle [28] that primed tensor quantities belong to the laboratory system \( L_i \), and unprimed tensor quantities belong to the sample coordinate system, \( S_j \). Once the lattice spacing, \( d_{\varphi\varphi} \), is obtained from the position of the diffraction peak for a given reflection \((hkl)\), the strain along \( L_3 \) may be obtained from the formula

\[
(e_{33})_{\varphi\varphi} = \frac{d_{\varphi\varphi} - d_0}{d_0} \tag{5.6}
\]

where \( d_0 \) is the unstressed lattice spacing. This strain can be transformed to the sample coordinate system \( e_{ij} \) by the following transformation tensor [29]

\[
(e_{33})_{\varphi\varphi} = a_{3k}a_{3l}e_{kl} \tag{5.6}
\]
where \( a_{3k}, a_{3l} \) are direction cosines between \( L_3 \) and \( S_k, S_l \) respectively. The direction cosine matrix for this case is

\[
a_{ik} = \begin{bmatrix}
cos \Phi \cos \Psi & \sin \Phi \cos \Psi & -\sin \Psi \\
-\sin \Phi & \cos \Phi & 0 \\
cos \Phi & \sin \Phi \cos \Psi & \cos \Psi
\end{bmatrix}
\]  

(5.7)

Substituting for \( a_{3k}, a_{3l} \) in (5.6),

\[
\left( \varepsilon_{33} \right)_{q_0} = \frac{d_{q_0} - d_0}{d_0} = \varepsilon_{11} \cos^2 \Phi \sin^2 \Psi + \varepsilon_{12} \sin 2\Phi \sin^2 \Psi \\
+ \varepsilon_{22} \sin^2 \Phi \sin^2 \Psi + \varepsilon_{33} \cos^2 \Psi \\
+ \varepsilon_{13} \cos \Phi \sin 2\Psi + \varepsilon_{23} \sin \Phi \sin 2\Psi.
\]  

(5.8)

Equation (5.8) is the fundamental equation of X-ray strain determination. It is linear in six unknowns, \( \varepsilon_{11}, \varepsilon_{12}, \varepsilon_{13}, \varepsilon_{22}, \varepsilon_{23}, \varepsilon_{33} \) and may be solved if \( d_{q_0} \) is measured in an appropriate number of independent directions.

If we assume biaxial stress (that is there is no strain in \( S_3 \)), then the strain tensor has the form

\[
\varepsilon_{ij} = \begin{bmatrix}
\varepsilon_{11} & \varepsilon_{12} & 0 \\
\varepsilon_{21} & \varepsilon_{22} & 0 \\
0 & 0 & \varepsilon_{33}
\end{bmatrix}
\]  

(5.9)
For such a strain tensor, equation (5.8) becomes

\[
\frac{d_{qp} - d_0}{d_0} = \left( \varepsilon_{11} \cos^2 \Phi + \varepsilon_{12} \sin 2\Phi + \varepsilon_{22} \sin^2 \Phi - \varepsilon_{33} \right) \sin^2 \Psi + \varepsilon_{33} \quad (5.10)
\]

which is linear if we plot strain against \( \sin^2 \Psi \).

### 5.4 Determination of Stresses from Diffraction Data

Once the strains are obtained, the stresses in the \( S \) can be calculated from the general form of Hooke’s Law.

\[
\sigma_{ij} = C_{ijkl} \varepsilon_{kl}, \quad (5.11a)
\]

or the other way around

\[
\varepsilon_{ij} = S_{ijkl} \sigma_{kl}, \quad (5.11b)
\]

where the \( C_{ijkl} \) and the \( S_{ijkl} \) refer to the \( S \) coordinate system.

If the material under investigation is isotropic, we can write (5.11b) as

\[
\varepsilon_{ij} = \frac{1 + \nu}{E} \frac{\sigma_{ij}}{\sigma_{ii}} - \frac{\nu}{E} \sigma_{kk} \cdot \quad (5.12)
\]
If the stress tensor in the irradiated layers is biaxial, using (5.12) in (5.8) one obtains

\[ \frac{d_{\phi}}{d_0} = \frac{1 + \nu}{E} \sigma_\phi \sin^2 \psi - \frac{\nu}{E} (\sigma_{11} + \sigma_{22}), \]

(5.13)

where \( \sigma_\phi \), the stress component along \( S_\phi \) direction (Figure 5.4) given by

\[ \sigma_\phi = \sigma_{11} \cos^2 \Phi + \sigma_{22} \sin^2 \Phi, \]

(5.14a)

or

\[ \sigma_\phi = \sigma_{11} \cos^2 \Phi + \sigma_{12} \sin \Phi + \sigma_{22} \sin^2 \Phi \]

(5.14b)

The stress in the \( S_\phi \) system can be directly calculated from the slope of the least-squares fitted line to the experimental data, measured at various \( \Psi \) if the elastic constants \( E, \nu \), and the unstressed plane spacing, \( d_0 \), are known.

By using the equation

\[ \frac{1}{2} s_2 = \frac{\nu + 1}{E} \]

(5.15)

where \( \nu \) is Poisson’s ratio and \( E \) is Young’s modulus, and equating the slope of the \( \sin^2 \psi \) curve to

\[ \text{slope} = \frac{1}{2} s_2 \sigma_\phi, \]

(5.16)

the residual stress can be derived as

\[ \sigma_\phi = (\text{slope}) \frac{E}{(\nu + 1)} \]

(5.17)

This procedure is known as the “\( \sin^2 \Psi \) stress determination” technique.
6 X-RAY MEASUREMENTS

The X-ray diffraction study is divided into two parts:

- **Phase analysis measurements**
  Phase analysis measurements were performed to find out the composition of the sample, to observe the copper and krypton peaks, and further with the aim to determine the lattice parameters for both copper and krypton. Since only crystalline materials have sharp peaks in their X-ray spectrum, one is able to find the lattice parameters of the sample under investigation, bulk Cu(Kr) sample in our case, by finding the precise 2θ positions of copper and krypton peaks. The BRUKER-AXS D8 ADVANCE diffractometer was used to perform the phase analysis measurements.

- **Stress determination**
  The second step in the measuring process is to determine the stress inside the Cu(Kr) sample. This was accomplished by means of the sin²θ residual stress measurement technique introduced in Chapter 3. The BRUKER-AXS D8 DISCOVER diffractometer was used for the stress measurements. This stress value is crucial in the long life stability of the sample. Here we recall that the residual stress was introduced into the Cu(Kr) sample by the sputtering / implantation process (see Chapter 2).

6.1 **Phase Analysis Measurement**

The aim of phase analysis measurements is to quantitatively determine the structural properties of any material, in this case both the krypton inside the copper matrix and the copper itself. Information regarding the presence, phase, packing density and
crystal structure of the krypton can be determined from accurate lattice parameter measurements.

Figure 6.1 The BRUKER-AXS D8 ADVANCE diffractometer used for phase analysis. Actual diffractometer is shielded inside the glass cabinet; the lower part contains the high-voltage generator and the control electronics.

The analysis was carried out using a BRUKER-AXS D8 ADVANCE (Figure 6.1) diffractometer at the regional X-ray facility at the National Accelerator Centre (NAC). Figure 6.1 shows the complete unit of the D8 ADVANCE diffractometer with the actual diffractometer at the centre. The D8 ADVANCE is a self-contained commercial unit with the lower part of the housing containing the high-voltage generator and control
electronics. The upper part, containing the diffractometer, is a shielded safety cabinet to prevent accidental exposure to X-rays. A personnel computer, used to control the whole unit and for data acquisition and analysis, is not shown in Figure 6.1.

A detailed view of the diffractometer with the sample stage of the D8 ADVANCE diffractometer is shown in Figure 6.2. The main features will be described here; details will be given in the discussion of Figure 6.3. The X-ray source is located in the tube housing (1) at the left of the picture. A collimated primary beam (see below) from the X-ray tube is diffracted from the sample (2) positioned at the centre of the two axes of the goniometer (3). The diffracted secondary beam is detected after the further collimation and monochromatisation (see below) by a scintillation counter (4).

Figure 6.2  D8 Diffractometer located in the upper part of the unit and shielded from outside by glass panels against an exposure of X-ray radiation:

(1) X-Ray source,

(2) Sample holder,

(3) Goniometer,

(4) Detector.
Figure 6.3 shows the beam path for the D8 ADVANCE X-ray diffractometer for the phase analysis measurement. Four different slits; a divergence slit in the primary beam side (A), an anti-scattering slit (B), monochromator slit (C) and detector slits (D) in the secondary side were used with a monochromator (M). The diffraction angle is given by the position of the two goniometer circles which are PC controlled. The divergence and anti-scattering slits were controlled by a PC, so that the irradiated area of the sample is kept constant during the \( \Theta-2\Theta \) scan. This mode is called the \textbf{v20 mode} in the Bruker-AXS manual [30].

![Diagram of beam path](image)

**Figure 6.3** Beam path of the D8 ADVANCE diffractometer set up for the phase analysis measurements.

1. X-ray source,
2. sample holder with sample,
3. goniometer not shown in Figure 6.3,
4. detector,
A. variable divergence slit (operated in v20 mode),
B. variable anti-scattering slit (operated in v20 mode),
C. monochromator slit,
D. detector slit,
M. monochromator.
For clearer representation of diffraction peaks, the $K_B$ reflections are suppressed using a monochromator. The monochromator of D8 ADVANCE is designed for the scintillation counters used in the detector. The graphite monochromator crystal has a lattice spacing of 2.708 Å and can be used with Cu, Cr, Fe and Mo X-ray radiation. [30]

In this measurement, the sample is kept horizontal at the centre of the goniometer (see Figure 6.2 and 6.3), using Bragg-Brentano geometry [31]. The Bragg-Brentano focusing geometry of the diffractometer is shown in Figure 6.4. In this geometry, the X-ray source and the detector are kept at the same distance from the sample, resulting in a focusing effect [31].

![Bragg-Brentano geometry](image)

Figure 6.4 Bragg-Brentano geometry. X-ray source and the detector lie equidistant from the sample surface, which results in a focusing effect.

$\Theta$ Glancing angle, $2\Theta$ Diffraction angle, $F$ Focus, $S$ Source, $P$ Sample [30]
The sample was mounted on the sample holder (2) by sticking with a piece of Prestik™ (rubber glue) and ensured that the sample surface is horizontal by levelling using direct the direct beam. For the direct beam levelling, one sets the X-ray source at $\Theta = 0^\circ$ and the detector at $\Theta = 180^\circ$ and levels the sample so that half of the direct beam passes through the sample and the other half hits the sample and is absorbed. A sharp cut in the detected X-ray spectrum ensures that the sample is horizontal and levelled at the same height with X-ray beams.

X-rays from the source (1) impinge on the specimen, which is on a holder (2) that can rotate around the goniometer axis (3) perpendicular to the plane of the diffractometer. The diffracted beam is then detected by the detector (4). The rotation of the source and the detector are through stepping motors and gear drives and can be positioned accurately within $\pm 0.0001^\circ$ [30] in $\Theta$.

The measurements were performed with 40 kV X-ray tube voltage and 40 mA X-ray tube current supplied from the high voltage generator located in the lower part of the D8 Diffractometer unit. 2$\Theta$ ranges for the measurement were 5 - 140$^\circ$ with a step size of 0.01$^\circ$ and measuring time of 6 s per step, with the total measurement time of 22.5 h. One can rotate the sample on the sample stage around the sample normal ($\Phi$ rotation), but this feature was not used in our measurements. The other set up parameters for the phase analysis are given in Table 4.1.

<table>
<thead>
<tr>
<th>X-ray voltage</th>
<th>40 kV</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-ray tube current</td>
<td>40 mA</td>
</tr>
<tr>
<td>Divergence slit</td>
<td>V20 mode (variable)</td>
</tr>
<tr>
<td>Anti-scattering slit</td>
<td>V20 mode (variable)</td>
</tr>
<tr>
<td>Detector slit</td>
<td>2.0 mm</td>
</tr>
<tr>
<td>Monochromator slit</td>
<td>0.1 mm</td>
</tr>
<tr>
<td>$\Theta$-2$\Theta$ step size</td>
<td>0.01$^\circ$</td>
</tr>
<tr>
<td>Time per step</td>
<td>6 s</td>
</tr>
<tr>
<td>$\Phi$ Rotation</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 4.1 D8 ADVANCE Diffractometer parameters for lattice parameter determination
6.2 **STRESS DETERMINATION**

The second step in the experimental process is to determine the stress in the matrix of the Cu(Kr) sample. The sputtering /implantation process (see Chapter 2) introduced krypton atoms into the copper matrix, which is expected to be the origin of the residual stress built up in the Cu(Kr) material. This is generally the case for both macro and micro residual stresses. The macro residual stress can be determined by the methods discussed in Chapter 4 which rely in the conventional “sin^2Ψ method”. No attempt was made to measure the stress state in the Kr precipitates because of the very low intensity of the diffraction peak. For a meaningful sin^2Ψ curve for Kr, a measurement time of about 2 months per data point would be required under the experimental setup described below.

![BRUKER-AXS D8 DISCOVER diffractometer used for sin^2Ψ stress determination.](image-url)
Stress determination was performed using the Bruker-AXS D8 DISCOVER diffractometer shown in Figure 6.5. The basic setup is similar to that of D8 ADVANCE described above. The main difference between the two diffractometers shown in Figure 6.5 and 6.1 is that in the D8 DISCOVER the two-axis goniometer is mounted horizontally and a third axis is included. This additional axis allows stress measurements in side inclination [21] mode to be performed.

The sample stage and the goniometer of the D8 DISCOVER diffractometer is shown in Figure 6.6. The basic operation of the diffractometer is the same as that discussed for the D8 ADVANCE above, with the X-ray beam from the source (1) being diffracted by the sample (2) and detected by the scintillation counter (4). The additional axis is provided by a quarter circle Eulerian cradle (3). The positioning of the sample is achieved by the re-positioning stages built into the sample holder. The sample is mounted on the stage by automatically by the vacuum pump of the machine.

Figure 6.6 Goniometer and the sample stage of the D8 DISCOVER diffractometer

1. X-Ray source,
2. sample holder,
3. Eulerian cradle mounted on a two axes goniometer,
4. Detector.
The D8 DISCOVER diffractometer set-up and beam path is illustrated in Figure 6.7. The two collimators A and B are functionally equivalent to the variable slits in the D8 ADVANCE (Figure 6.3), except that here a narrow point focus is required. The divergence slit A is therefore replaced by a pinhole and collimator arrangement, which restricts the illuminated spot on the sample to $\approx 1$ mm diameter at normal incidence. The Soller slit B, in the secondary path, which replaces the anti-scatter slit, consists of long parallel vanes that restrict the divergence of the beam. The monochromator in the D8 ADVANCE is replaced by a Ni filter which serves to absorb most of the CuK$_\beta$ radiation. A Soller slit of 0.4° and a 15 $\mu$m Ni filter were used. The scheme shown in Figure 6.7 is not drawn to scale, but it was drawn to make the different items in the beam path clear, e.g. the divergence collimator is mounted on the X-ray tube housing in the actual diffractometer.

Figure 6.7 Beam path for the D8 DISCOVER diffractometer

(1) X-ray Source
(2) sample holder / sample,
(3) detector,
(A) pinhole collimator,
(B) Soller collimator,
(M) Ni filter.
Stress determination measurements can be carried out either as $\Omega$ or $\Psi$ goniometer measurements, which are also known as iso-mode or side inclination mode. In the $\Omega$-goniometer mode, one tilts the sample so that the sample surface normal is on the same plane with the incoming and outgoing beams while in the $\Psi$-goniometer the sample surface normal is off the plane of the X-ray beams, keeping the incident beam angle constant (Figure 6.8).

In the side inclination mode, the tilts are around an axis parallel to the plane of the diffractometer and the incident and diffracted beams have the same path length independent of the $\Psi$-tilt.

For the stress determination, the 111 diffraction peak of the copper matrix was used. With CuK$\alpha$ radiation, a diffraction pattern in $2\theta$ interval between $2\theta = 42.5^\circ$ and $2\theta = 44.5^\circ$ was recorded. The step size for the $2\theta$ angles was 0.01°, to determine the peak position accurately.
Measurements were taken for nine \( \Psi \)-tilts between 0 and 80° in 10° intervals. The measurement times were longer for the higher \( \Psi \) angles because the intensity decreases highly with increasing \( \Psi \) tilting. The total running time for stress determination measurements is well over a week. All the measurement parameters are summarized in Table 6.2.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-ray tube potential</td>
<td>40 kV</td>
</tr>
<tr>
<td>X-ray tube current</td>
<td>35 mA</td>
</tr>
<tr>
<td>Filter</td>
<td>Ni Filter (15( \mu )m)</td>
</tr>
<tr>
<td>Soller slit</td>
<td>0.4°</td>
</tr>
<tr>
<td>Divergence slit</td>
<td>0.3°</td>
</tr>
<tr>
<td>( 2\theta )</td>
<td>42.5 - 44.5</td>
</tr>
<tr>
<td>Step size</td>
<td>0.01</td>
</tr>
<tr>
<td>Step time</td>
<td>170 s for ( \Psi = 10,20,30,40 ) 300 s for ( \Psi = 50,60,70,80 )</td>
</tr>
<tr>
<td>( \Psi )-tilting</td>
<td>10,20,30,40,50,60,70,80°</td>
</tr>
</tbody>
</table>

Table 6.2 D8 DISCOVER Diffractometer parameters for stress determination

Calibration for misalignment of the stress diffractometer was obtained from the measurements on stress free tungsten powder under the same conditions as for the Cu(Kr) sample. The measurements for the stress determination in the copper matrix of the Cu(Kr) sample were performed under identical conditions.
7 RESULTS

The experimental results of the phase analysis and the stress determination will be discussed separately in this chapter and both results will be combined in the discussion, in the next chapter.

7.1 PHASE ANALYSIS

The output for the phase analysis measurements is a $2\theta$ scan of the diffracted X-ray intensity, which contains different peaks corresponding to different families of lattice planes in the polycrystalline material. From the distribution of the peaks the different phases present in the sample can be identified. Furthermore, accurate determination of the peak positions can be used to calculate the lattice parameters of the phase under investigation.

The full diffraction pattern for the phase analysis measurement of Cu(Kr) sample is given in Figure 7.1, showing the raw data. The horizontal axis shows the $2\theta$ angle in degrees, and the vertical axis shows the relative intensity of the diffracted beam. This intensity is the total detected X-ray counts at that particular $2\theta$ angle in the range given by the step size integrated over one time step. (Typical steps are 1–2 s and 0.01°. See Table 6.1). These peaks are labelled in the figure, and a comparison of the measured peak positions with the literature will be given below in Table 7.1. An eighth peak with a very low intensity is scarcely noticeable at a $2\theta$ angle of 82°. This can be attributed to the only krypton diffraction peak visible on this scale. In Figure 7.1, only the peaks corresponding to the strong diffracted intensity from the Cu matrix (which makes up the 98% of the material) are easily visible.
Figure 7.1 Full diffraction profile the $\Theta$-2$\Theta$ scan of the copper-krypton sample, range: 5-140°. The raw data file for phase analysis with Cu-K$_\alpha$ radiation. The copper peaks are marked with arrows. A table of all of copper peaks and corresponding Miller indices is listed in Table 7.1 The krypton peaks are not easily visible on this scale, but one diffraction peak at 82° can be identified, which doesn’t belong to the copper spectrum, and is marked with a dashed arrow.

The measured 2$\Theta$ range, 5 - 140°, contains seven of the eight diffraction peaks of copper listed in the powder diffraction file [31]. The peak positions for copper and the statistical errors in peak determination are given in Table 7.1 along with the values given by the powder diffraction file.

Figure 7.1 shows the raw data acquired during the experiment. The raw data are then corrected for background and CuK$_\alpha_2$ subtraction and afterwards smoothed using the manufacturer’s proprietary software, DIFFRAC$\text{plus}$ [32].
The background correction eliminates the scattering intensity, which does not contribute to the diffraction line. A constant or constant background is always present in the raw diffraction patterns, but this is easily removed leaving the diffraction peaks ready for further investigations.

<table>
<thead>
<tr>
<th>Lattice planes of copper</th>
<th>Peak position from powder diffraction file (Degrees)</th>
<th>Measured peak position 2Θ (Degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>43.298</td>
<td>43.284 ± 0.05</td>
</tr>
<tr>
<td>200</td>
<td>50.434</td>
<td>50.407</td>
</tr>
<tr>
<td>220</td>
<td>74.132</td>
<td>74.083</td>
</tr>
<tr>
<td>311</td>
<td>89.934</td>
<td>89.881</td>
</tr>
<tr>
<td>222</td>
<td>95.143</td>
<td>95.085</td>
</tr>
<tr>
<td>400</td>
<td>116.849</td>
<td>116.849</td>
</tr>
<tr>
<td>331</td>
<td>136.287</td>
<td>136.287</td>
</tr>
<tr>
<td>420</td>
<td>144.432</td>
<td>Not measured</td>
</tr>
</tbody>
</table>

Table 7.1 *Comparison of measured diffraction peak positions using CuKα radiation and the powder diffraction file data for copper. The 420 peak is not the measured 2Θ = 5-140° range.*

Another artefact arises from the presence of CuKα₂ X-rays in both the primary and the diffracted beams. The Kα₂ radiation is present in the incident spectrum because the X-ray source is not purely monochromatic, and this leads to additional peaks, which may overlap the peaks due to Kα₁. The Kα₂ subtraction procedure scans the full spectrum and eliminates the scattered intensity due to the Kα₂ radiation of the X-ray tube from the measured intensity distribution. A modified Rachinger function [33,34] is applied to all intensities between the left and right background positions to eliminate the Kα2 components.
Finally the diffraction pattern is smoothed using DIFFRAC<sup>plus</sup> software to reduce the effects of counting statistics on the result of background and $K\alpha_2$ correction and calculation of the peak position. The DIFFRAC<sup>plus</sup> smoothing procedure uses a Savitzky-Golay digital filter [33,35].

Figure 7.2 illustrates the same diffraction pattern on an expanded scale, showing the peaks, which are not easy to distinguish on the scale of Figure 7.1. The intensity of the krypton peaks are not as large as copper because the krypton fraction is only 2-3 at %. We can easily distinguish four krypton peaks which appear before and in between the copper peaks. The krypton peaks are marked with arrows in the figure. Figure 7.2 is an expanded version of the raw data and the diffraction pattern is corrected for background, $K\alpha_2$ and smoothed afterwards, as discussed above.

Figure 7.2 Diffraction pattern of the expanded scale of Figure 7.1 clearly showing the four Kr diffraction peaks. The intensity of the krypton peaks are far less than the copper peaks due to the less diffraction from the small fraction of krypton (2 at %) inside the bulk copper-krypton sample. The krypton peaks are marked with arrows.
Both the copper and the krypton peaks can be seen clearly in the Figure 7.2. Since each diffraction peak has generally a broad intensity distribution, its position must be determined by a suitable peak location method. Different methods are available; the centre of gravity method [36], functional representation of X-ray peaks by matching a function to the observed peak profile [28] and peak determination by fitting a parabola to diffraction peak data [37]. The centre of gravity method is used in DIFRAC$^{\text{plus}}$ software for peak determination.

A comparison of the measured copper peaks and the powder diffraction file data (Table 7.1) shows that all copper peaks in the measured range can be observed. The measured peak position given in table 7.1 can be used to determine the lattice parameter of the Cu in the matrix. The lattice spacing for each peak can be easily calculated by using Bragg’s law (5.3). From this the lattice parameter $a$ of the fcc copper lattice can be calculated from

$$a = d\sqrt{h^2 + k^2 + l^2}$$  \hspace{0.5cm} (7.1)

where $h$, $k$ and $l$ are the Miller indices of the Bragg reflection.

Finally, the lattice parameter can be taken as the average of the seven individual values calculated for each lattice plane (hkl). The lattice parameter for copper in the matrix of the Cu(Kr) sample is found to be $3.617 \pm 0.010 \text{Å}$. This value is slightly smaller than, but within 0.01% of the powder diffraction file value $3.6178 \text{Å}$.

<table>
<thead>
<tr>
<th>Peak</th>
<th>2-theta</th>
<th>Counts</th>
<th>Relative intensity Measured (%)</th>
<th>Relative intensity PDF Data (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>43.30</td>
<td>84000</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>200</td>
<td>50.43</td>
<td>16500</td>
<td>20</td>
<td>46</td>
</tr>
<tr>
<td>220</td>
<td>74.13</td>
<td>5500</td>
<td>7</td>
<td>20</td>
</tr>
<tr>
<td>311</td>
<td>89.93</td>
<td>4500</td>
<td>5</td>
<td>17</td>
</tr>
<tr>
<td>222</td>
<td>95.14</td>
<td>5000</td>
<td>6</td>
<td>5</td>
</tr>
<tr>
<td>400</td>
<td>116.92</td>
<td>1500</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>331</td>
<td>136.51</td>
<td>2200</td>
<td>3</td>
<td>9</td>
</tr>
<tr>
<td>420</td>
<td>144.72</td>
<td>Not measured</td>
<td>-</td>
<td>8</td>
</tr>
</tbody>
</table>

Table 7.2 Comparison of measured intensity of the copper diffraction peaks with the values give in the powder diffraction file
The diffraction peak intensities are also compared with the powder diffraction files in Table 7.2 and Figure 7.3. The relative intensities of the measured copper peaks compared with the powder diffraction data change from one set of Miller indices to another, which indicates some texture in the sample. The 111 peak intensity is taken to be 100% and the other peaks are normalized accordingly, for both the measured diffraction patterns and the PDF file values.

![Figure 7.3](image)

Figure 7.3 *Intensity comparison of the measured copper peaks ( ) with the PDF data ( ). The relative intensities vary indicating the presence of texture*

Determination of the structure and the lattice parameter of the krypton precipitates is more difficult because it is not straightforward to analyse the weak krypton peaks and, in addition, we do not know the crystal structure of the krypton in the precipitates. Four peaks, which cannot be attributed to copper, can clearly be seen. It may be assumed these peaks are due to krypton. The 2Θ positions for these peaks are determined by the same procedure discussed above for the copper peaks and are listed in Table 7.3.
<table>
<thead>
<tr>
<th>Krypton peak positions (2θ degrees)</th>
<th>hkl</th>
<th>Lattice spacing ( d (\text{Å}) )</th>
<th>Lattice parameter ( A (\text{Å}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>29.40</td>
<td>111</td>
<td>3.03782</td>
<td>5.2617</td>
</tr>
<tr>
<td>82.05</td>
<td>420</td>
<td>1.17431</td>
<td>5.2740</td>
</tr>
<tr>
<td>98.36</td>
<td>333</td>
<td>1.0182</td>
<td>5.2924</td>
</tr>
<tr>
<td>121.56</td>
<td>442</td>
<td>0.88318</td>
<td>5.2991</td>
</tr>
</tbody>
</table>

Table 7.3 *Krypton peaks and lattice parameter determination*

We have to solve the reverse problem and find possible \( hkl \) values, which would reproduce the measured lattice spacings. The main problem is that we have to try different \( hkl \) values and check if for any lattice parameter the observed four peaks can be located within reasonable errors. One should also bear in mind the possibility that some low-intensity peaks may not be observed because the effect of texture discussed above.

The lattice parameter \(<a> = 5.282 \pm 0.015 \text{ Å}\) and the \( hkl \) values 111, 420, 333 and 442 locate the krypton peaks very precisely. Since the \( hkl \) values for the peaks are either all even or odd, it can be concluded that the krypton precipitates inside the copper have the same fcc structure at room temperature.

### 7.2 Stress Determination

The macro residual stresses were determined with the \( \sin^2 \Psi \) technique described in Chapter 5 using the 111 peak of copper. In Figure 7.4 two diffraction peaks of the 111 reflection are shown for \( \Psi = 0^\circ \) (Figure 7.4a) and \( \Psi = 70^\circ \) (Figure 7.4b). A complete set of the diffraction peaks can be found in Appendix.
Figure 7.4 111 diffraction peak from the copper matrix of the Cu(Kr) sample using CuKα radiation for ψ tilts of (a) 0 and (b) 70°. The data have been corrected for background and Kα₂ and smoothed afterwards.
The same background, $K\alpha_2$ and smoothing operations are performed as described in section 7.1 on the data for the 111 peak used in the stress determination for all $\Psi$ angles.

Peak determination was carried out using the DIFFRAC$^{\text{plus}}$ package. The centre of gravity method, described in section 7.1 above, was used for peak location determination.

Figure 7.5 $\sin^2 \Psi$ curve for the 111 peak of copper matrix of the Cu(Kr) sample.

The $\sin^2 \Psi$ curve shows an oscillation rather than a slope for the Cu(Kr) sample. There is either no slope or a slope that is very small. By using conventional least-squares methods, one can associate linear fit ($mx + b$) to the points with $m = -1.97 \times 10^{-5}$, $b = -5.48 \times 10^{-5}$. The error in the slope is much higher than the slope and this actually confirms that there is no slope but an oscillatory behaviour of the $\sin^2 \Psi$ curve.
The oscillatory behaviour of the $\sin^2\Psi$ curve tells us that there is a strong texture inside the sample, which also agrees with the intensity comparisons in the phase analysis measurements.

Inserting the numerical values of Poisson's ratio $\nu=0.34$, Young's modulus, $E=129$ GPa, [38] and the slope into equation (5.17), a stress value of $\sigma_{\phi} = -1.8 \pm 40$ MPa was determined. In other words there is very small or no macro residual stress present in the Cu matrix.
8 DISCUSSION

In this chapter the results of the X-ray diffraction experiments are briefly explained and the implications of both phase analysis and stress determination measurements will be discussed.

The phase analysis measurements clearly show the presence of krypton diffraction peaks as well as the copper peaks (Figure 7.1, Table 7.1, Table 7.3). This result confirms that krypton precipitates are solidified inside the copper matrix during the implantation/sputtering process (see chapter 2). Thus there are still solid krypton precipitates at room temperature inside the copper matrix after 20 years of storage. Since the liquefaction or solidification of rare gases at room temperature requires high pressures (~20–30 kilobar [39]), the presence of solid krypton in bubble form gives a hint of the huge stress the matrix suffers.

Furthermore, lattice parameter calculations for the copper matrix and krypton bubbles were performed by using clearly distinguishable X-ray diffraction peaks of copper and krypton, respectively. The copper matrix has a lattice parameter of $a = 3.6170 \pm 0.010 \, \text{Å}$. A comparison with the powder diffraction file data [40] value of 3.61500 Å yields the information that the measured/calculated lattice parameter is slightly, 0.06%, larger than the stress free powder sample.

The same lattice parameter calculations give a value of $a = 5.282 \pm 0.015 \, \text{Å}$ for the krypton precipitates, while the literature value is nearly 10% greater at 5.68 Å [32]. It is not straightforward to raise a conclusion from this, because the literature value is obtained at much colder temperature, at 82K and at atmospheric pressure. The lattice structure for krypton bubbles is found to be fcc.

More information about the copper matrix can be obtained from the stress determination measurements. The results of the stress determination confirm that there is negligible
macro residual stress inside the copper matrix. The very slight slope of the \( \sin^2 \Psi \) curve indicates a macro residual stress of \(-1.8 \pm 40\) MPa. Actually there is hardly a slope in the \( \sin^2 \Psi \) curve, but there is an oscillatory behaviour which is due to the texture present in the copper matrix, which we already know from the diffraction peak intensity distribution Figure 7.3.

At this point the results of the experiments can be summarised as:

- krypton bubbles inside copper matrix solidify with an fcc structure,
- the lattice parameter of krypton is \( a = 5.282 \pm 0.015 \) Å, and
- there is no macro residual stress in the copper matrix

The following critical question will be answered in the next section:

- What is the reason that the solid krypton bubbles are stable inside the copper matrix for a long period of time and that there is no macro residual stress determined in the matrix?

To determine the mechanical state of the copper matrix due to the krypton bubbles; we have to determine the pressure inside the krypton bubbles and calculate the shear stress of the matrix by using the Mott & Nabarro inclusion method (see Chapter 4).

The pressure of the krypton bubbles can be determined by two alternative methods from previous authors’ works. Firstly with the help of P-V-T data for krypton calculated from Ronchi’s equation of state [39], and secondly and less precisely from experimental data of the lattice parameter versus pressure, determined by X-ray diffraction and energy-dispersive extended X-ray absorption fine structure spectroscopy (EXAFS) [41].

### 8.1 Ronchi Equation of State

The behavior of noble gases at high densities deviates from the Van Der Waals equation of state due to the increasing atom-to-atom interactions. Ronchi [41] investigated a new equation of state for argon, krypton and xenon at high densities and high temperature in

The Ronchi paper tabulates the results in a P-V-T table where the pressure of the noble gases are given in relation to their molar volume, for high densities like close packing, and from room temperature up to 2300 K (see Appendix B).

To determine the pressure in the krypton bubbles from the Ronchi P-V-T data the molar volume of the krypton bubbles in the bubbles is required. The molar volume is easily calculated from the lattice parameter. Since krypton's structure is fcc, there are 4 atoms per unit cell. Then

$$\text{Volume per atom} = \frac{\text{Volume of unit cell}}{\text{Number of atoms per unit cell}} = \frac{a^2}{4}$$

(8.1)

where \(a\) is the lattice parameter of the krypton. The molar volume is then

$$\text{Molar volume} = \frac{a^3}{4} N_A = \frac{(5.2882\text{Å})^3}{4} \times 6.02 \times 10^{23} = 22.15\text{cm}^3\text{/mol}$$

(8.2)

where \(N_A=6.02 \times 10^{23}\) is Avagadro's number.

Using the Ronchi equation of state with molar volume of 22.15 cm\(^3\)/mol and room temperature, a pressure of 2.6 \(\pm\) 0.1 GPa is found by interpolation.

### 8.2 Experimental Pressure vs. Lattice Parameter Data

The second method is based on experimental data gathered from energy-dispersive extended X-ray absorption fine structure spectroscopy (EXAFS) methods. Polian et al. investigated the high-pressure krypton lattice parameters in a diamond anvil cell at room temperature [41]. The equation of state agrees very well with diffraction data. The pressure dependence of the Debye-Waller factor was determined by Polian et al. and
compared with calculations using pair potentials. By using X-ray absorption near-edge structure part of the spectrum shows the possibility of measuring the pressure in bubbles of krypton implanted in metallic matrices (Figure 8.1).

![Graph](image)

Figure 8.1 *Comparison of the pressure dependence of the lattice parameter determined by X-ray diffraction (squares) and EXAFS (stars).* From [40]

With these two alternative methods results we can conclude that the copper resists a pressure of 26600 bar to hold the krypton bubbles inside the matrix. To get an impression of the magnitude of this pressure - a pressure that can solidify gases - it corresponds to the hydrostatic pressure a diver would experience at a depth of about 260 km. This is over 20 times as deep as the deepest ocean bed!

As discussed above, the matrix must sustain a pressure of about 26000 bar to contain the krypton bubbles. At first sight this seems to be impossible, if it is taken into account, that copper is known as one of the most ductile metals. That only shear stresses are present in the matrix is confirmed with the macro residual stress determination which is not
The pressure in the bubbles at the bubble-matrix interface is balanced with the shear stress suffered by the matrix. In Chapter 4 the relation between the pressure in the bubbles and the shear stress in the matrix was calculated. The shear stress at the interface turns out to be one-quarter of the bubble pressure. By applying equation (4.21) we obtain a maximum shear stress in the matrix, directly at the matrix-bubble interface, of only 665 MPa.

The pressure is maximum at the matrix-bubble interface and decreases rapidly with distance from the precipitate with $\frac{1}{r^3}$ law (Eq. 4.20). This stress value is far smaller than the theoretical yield strength of single crystalline copper in the absence of dislocations, which is approximately $\frac{G}{\delta}$ [42,43] where $G$ is the shear modulus. It is also similar to the macroscopic yield strength of many technical copper alloys [44] thus explaining the long-term stability of the krypton bubble-copper matrix systems.
9 CONCLUSION

We have studied a bulk Cu(Kr) sample, which was produced by a special implantation/sputtering process developed to introduce bulk volumes of krypton gas inside the copper metal. The Cu(Kr) sample is distinctive in the sense that it contains a high number of krypton bubbles inside the copper matrix distributed throughout the volume of the sample.

The sample was studied by means of X-ray diffraction techniques. The X-ray experiments confirm that krypton forms solid precipitates inside the copper matrix and that they are stable inside the matrix for a long period; in this case 20 years. Furthermore we have shown that the krypton precipitates have the same fcc structure as the host copper. The solid krypton in the bubbles has a lattice parameter of 5.28 Å. A pressure of 2.6 GPa is associated with the lattice parameter, by using two different methods, which is consistent with estimates of previous authors [39, 41].

The X-ray diffraction experiments revealed critical results about the residual stress inside the copper matrix. The results indicate that the matrix is free from normal macro residual stress, confirming the predictions of elasticity theory which predict that the matrix experiences only shear strain. The magnitude of this shear stress is estimated from the bubble pressure to be below the theoretical yield stress of the matrix in the absence of dislocations, thus explaining the long-term stability of the bubbles.

This work supplied a sound background for further research in the area. The mechanical properties of the sample can be further investigated to include the micro stresses inside the material. Future work can and should investigate the thermodynamic and electronic properties of this unusual material, which can lead to better understanding of extreme materials and open doors for exciting new applications, e.g. solid state electronics.
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INVESTIGATION OF KRYPTON BUBBLES IN COPPER USING X-RAY TECHNIQUES

Mecit Yaman

Thesis submitted in partial fulfilment of the requirements for the degree of

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7 December 2001
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At last, I want to devote this thesis to my All-Knowing Allah. I thank Him for giving me good parents and friends. It would not have been possible to complete this master's program without His grace.
<table>
<thead>
<tr>
<th>Reference</th>
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<th>Title</th>
<th>Publisher/Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>[27]</td>
<td>A.E. Love</td>
<td>Theory of Elasticity, 1927</td>
<td></td>
</tr>
<tr>
<td>[33]</td>
<td>DIFFRAC+ STRESS 1.0</td>
<td>Residual Stress Determination USER’S MANUAL, BRUKER AXS, INC ANALYTICAL X-RAY SYSTEMS, Germany</td>
<td></td>
</tr>
</tbody>
</table>


APPENDIX A

This appendix contains the complete set of 111 diffraction peaks from the copper matrix of the Cu(Kr) sample using CuKα radiation for Ψ tilts of from 0° to 80°. The horizontal axis is the diffraction angle 2θ.

Ψ=0°

Ψ=10°
$\Psi = 20^\circ$

$\Psi = 30^\circ$
## APPENDIX B

This appendix contains the p-V-T data for krypton; the entries are the volume in cm³/mol (row at the top) and the temperature in K; the volumes correspond to equal steps of reduced density from 0.1 to 2; the pairs in the table correspond to the value of compressibility Z (top) and the pressure in bar (bottom), see [39].

<table>
<thead>
<tr>
<th>p-V-T data for krypton: entries as in table 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>286.5</td>
</tr>
<tr>
<td>0.94</td>
</tr>
<tr>
<td>73</td>
</tr>
<tr>
<td>0.94</td>
</tr>
<tr>
<td>1.04</td>
</tr>
<tr>
<td>0.99</td>
</tr>
<tr>
<td>1.34</td>
</tr>
<tr>
<td>1.02</td>
</tr>
<tr>
<td>1.77</td>
</tr>
<tr>
<td>1.04</td>
</tr>
<tr>
<td>212</td>
</tr>
</tbody>
</table>

Note: The table entries are volumes in cm³/mol and temperatures in K.