A HIGH RESOLUTION POSITRON ANNIHILATION STUDY IN THE  $\alpha$ -PHASE REGION OF THE COPPER GALLIUM AND COPPER GERMANIUM SYTEMS

by

JAMES GORDON McLARNON

B.Sc., University of Alberta, 1963

M.Sc., University of Alberta, 1965

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#### ABSTRACT

A high resolution positron annihilation angular distribution study has been made of a sequence of  $\alpha$ -phase alloys of copper gallium and copper germanium up to electron per atom ratios of about n = 1.25. While the primary study has concerned the variation of the radius of the neck features of the Fermi surface with electron concentration, data has also been obtained for the <110> Fermi cut-off for all alloys and in addition a <100> cut-off has been obtained for the highest concentration copper gallium alloy.

The two concentrated alloy systems show different behavior which is in agreement with low concentration studies done on CuGa and CuGe by Coleridge and Templeton. The CuGa neck radius if found to increase at a more rapid rate than predicted by rigid band theory, particularly at the highest concentration studied, whereas the CuGe behavior is below the rigid band predictions. General consistency is obtained between the neck variation and the <110> cut-off change. For the most concentrated CuGa alloy the results allow us to sketch a tentative Fermi surface and also provide convincing proof that the Fermi surface is most unlikely to contact the (200) Brillouin zone boundary even at the limit of the a-phase. This refutes the explanation given by Hume-Rothery and Roaf to account for the occurrence of the Hume-Rothery rules.

The present results are compared with the other existing experimental data for these alloys, in particular the optical absorption data of Montgomery and Pells, and it is concluded that, while it is not possible to make any definitive theoretical statements from the present data, the two different measurements provide complementary details of the alloy band

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structure which would serve as an excellent test of any theory. The recent calculations of Das and Joshi using the coherent potential model has had reasonable success in explaining the optical data for the α-phase of the copper zinc system and it is hoped that the present work will stimulate the application of such theory to the CuGa and CuGe systems.

üi

## To my mother and father

. IV

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#### CHAPTER I

#### INTRODUCTION

The positron annihilation experiment has become an important tool in the study of the momentum distribution of electrons in solids. The momentum distribution of the conduction electrons can be related to the Fermi surface and thus is of considerable importance in the study of metal physics. In particular, the technique of positron annihilation has been successfully applied to concentrated alloy systems which are inaccessible to experimental methods requiring that the electronic states be sufficiently long lived before collisions with impurity atoms occur. To a great extent previous positron annihilation experiments have been carried out on known Fermi surfaces to substantiate the reliability of the method. From these experiments, the limitations and abilities of the technique have been evaluated, leading to a further degree of sophistication in the application. The ability to ascertain specific features of the Fermi surface of metals, such as the contact with Brillouin zone boundaries, has been enhanced through the use of different detector geometries. These geometries, which greatly determine the resolution of the system, refer to the apertures preceding the detectors which count the gamma radiation resulting from an electron-positron annihilation.

By applying the conservation of momentum law to the annihilation it can readily be shown that the transverse momentum of the electronpositron pair is related to the deviation of the gamma pair from 180°. If the angular deviation is denoted by  $\theta$  and the transverse momentum by  $P_{+}$  then  $P_{+} = mc\theta$ . If one set of detectors is moved so that the angle  $\theta$  is varied, then an angular distribution can be plotted for P<sub>t</sub>. Further, if the positron momentum is assumed small compared to the electron momentum, the angular distribution will directly reflect the behaviour of the transverse momentum of the conduction electrons. Thus the positron annihilation technique is able to ascertain the momentum distribution of the conduction electrons in k space and information regarding the Fermi surface of the material can be garnered.

Generally speaking, most positron annihilation experiments make use of radio-active sources such as sodium-22 for the positron. In this case additional apparatus in the form of a magnet and stable power supply are needed to focus the positrons onto the sample. This type of experiment places a great dependence on the surface of the sample to be studied since the penetration depth of the positron is small.

A copper alloy can be studied in a different and more effective manner. If the abundant isotope of copper, atomic weight 63, is placed in a neutron flux then a reaction takes place which produces a radioactive isotope of copper with atomic weight 64. This isotope possesses a half life of 12.7 hours and undergoes radio-active decay with the emission of a positron. The resultant annihilation of the positron with an electron depends on the volume rather than the surface of the sample since positrons are produced throughout the sample. The source of neutrons in the present experiment is the Atomic Energy reactor at Chalk River, Ontario. The samples are irradiated for a period of three days and subsequently possess about 600 milli-curies of positron activity.

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The essence of the present experiment is the application of one particular geometry to the study of copper gallium and copper germanium alloy systems. This experiment was motivated by previous study of copper zinc (Williams, 1968) since gallium and germanium follow zinc in the periodic table with the addition of one and two 4p electrons respectively. Alloys of 3.3, 6.0 and 8.2 atomic percent germanium and 4.9, 8.7 and 12.7 atomic percent gallium were studied. The Fermi surface of copper has been previously determined (Pippard, 1958) and is found to consist of neck regions in the <111> crystallographic directions where the Fermi surface has made contact with the Brillouin zone boundary. In the present experiment the neck was used as a monitor in the study of the different copper alloys to ascertain the effects of adding a different number of conduction electrons to the intrinsic copper. The region corresponding to the location of the Fermi surface boundary in the <110> direction was also studied in order to plot Fermi surface contours for the alloys and observe the contribution of core electron states to the annihilation process. A single run to determine the <100> cut-off for the highest electron per atom ratio alloy was also undertaken.

As a background for the present experiment the nearly free electron theory, orthogonalized plane wave theory, and the augmented plane wave theory are discussed under the general heading of electrons in metals. In particular, the treatment of the augmented plane wave theory will lead to calculations for the band structure of copper: This chapter is also used to derive or explain such fundamental concepts as momentum space, Fermi surface, and Brillouin zone boundary so that the later reference may be made to them.

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The transition from the study of pure metals to the behaviour of concentrated, disordered, alloys is exceedingly difficult. As well as the inapplicability of the usual high powered experimental techniques to concentrated alloys, the loss of the inherent periodicity of the metal severely complicates the theoretical calculations. A simple approach in this study is to assume that the band structure of the host is not altered in the alloying process and that the introduction of impurity electrons can be accounted for by simply scaling the Fermi energy according to the electron per atom ratio. This rigid band model would be expected to possess some validity for dilute alloys, however Stern (1969) has indicated that the rigid band model may be applicable to concentrated noble metal alloys. This applicability is due to the large separation between the conduction bands for the noble metals and is related to the shielding effect of conduction electrons about solute atoms.

The only detailed theoretical model which has had success in accounting for the properties of disordered alloys is the coherent potential method of Soven (1966). The complexity of the problem is evident from the nature of the potential which is energy dependent and further, has an imaginary part to account for the damped wave functions characteristic of disordered systems. The coherent potential model has been applied to the copper zinc system by Soven (1966) and Das and Joshi (1972) with marked success in describing optical data for that alloy. It is hoped that the present measurements will stimulate a similar analysis of the copper gallium and copper germanium systems.

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Various conclusions can be drawn from the present data. For example the measurements of the alloy neck radii and Fermi surface cut-offs can be related to changes in the pure copper band structure with alloying. It should be stressed however, that the application of present measurements to band structure considerations is severely limited by such effects as the strong d band-conduction band interaction in copper. The experimental data can, however, be used to plot Fermi surface contours for the alloys which will be extremely useful in subsequent band calculations as applied to concentrated alloys. As well, the present work is relevant to the Hume-Rothery rules and leads to a definitive statement concerning the  $\alpha$ - $\beta$  phase transition in the copper gallium system. A comparison of the experimental work with other methods applicable to noble metal alloys serves as a useful summary of the current knowledge of the copper alloy system.

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#### CHAPTER II

#### ELECTRONS IN METALS

### A. Nearly Free Electron Theory

The present chapter includes a study of some of the common methods for studying the band structure of pure metals. A survey of the various methods will help to elucidate the band structure of copper and serve as an introduction to the study of copper alloy systems.

The simplest approach to study the behavior of conduction electrons in metals is to assume that the electrons are a gas of noninteracting particles moving in a constant potential. If the wave function of the conduction electrons is denoted by  $\psi$  the Schrodinger Equation is written

$$-\frac{\hbar^2}{2m}\nabla^2\Psi: \mathcal{E}\Psi \qquad 2-1$$

The solution to this equation for the wavefunction  $\psi$  and energy  $\varepsilon$  can easily be found by imposing the boundary conditions that the electrons occupy a cube of side L. The solutions are;

$$\Psi_{\underline{k}}(\underline{r}) = \int_{VI3}^{L} c^{i\underline{k}\cdot\underline{r}}$$

 $\mathcal{E}_{h}: \frac{h^{2}h^{2}}{2m}$ 

. •\_ 2-2

2-3

The electron wave functions are plane waves with index k, the wave number. The energies fill up k space such that at zero degrees Kelvin all states below  $\varepsilon_k = \varepsilon_f$  are occupied. The energy  $\varepsilon_f$  is known as the Fermi energy and the region enclosed by the boundary comprises occupied k space.

The free electron theory explains many general features of the electronic behavior in solids quite well but often fails to explain specific features such as the deviation of the Fermi surface from sphericity for many metals. The reason for this is that the assumptions underlying the theory do not correspond with the realistic situation. In reality the electron will move in a potential due to the ions and the other electrons in the crystal. This potential  $V(\underline{r})$  will be periodic in nature because of the regularity of the crystal lattice structure and consequently may be expanded in terms of reciprocal lattice vectors G;

$$V(\mathbf{r}) = \sum_{\mathbf{G}} V_{\mathbf{G}} \mathbf{e}^{i \mathbf{G} \cdot \mathbf{r}}$$
 2-4

If the wave functions of the system are labelled by  $\psi_k(\underline{r})$  then

$$\gamma_{\underline{k}}(\underline{r}) = e^{i\underline{k}\cdot\underline{r}} U_{\underline{k}}(\underline{r}) \qquad 2-5$$

where the periodic function  $U_{\underline{k}}(\underline{r})$  is invariant under a lattice translation  $\underline{r}$  so

$$J_{\underline{k}}(\underline{r}) = U_{\underline{k}}(\underline{r} + \underline{r})$$
2-6

The electron wave functions, which are plane waves in the free electron theory are modified by the periodic function  $U_{\underline{k}}(\underline{r})$  and are termed Bloch waves. Provided that  $V(\underline{r})$  is weak the free electron energy  $\varepsilon_0(k)$  given by equation 2-3 is modified by perturbation theory so that the nearly

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free electron energy  $\boldsymbol{\epsilon}_k$  is given by

$$E(\underline{R}) = E_0(\underline{R}) + \langle \underline{R} | W_m | \underline{R} \rangle + \sum_{\underline{R}} \frac{|\langle \underline{R} | V(\underline{r}) | \underline{R}' \rangle|^2}{E_0(\underline{R}) - E_0(\underline{R}')} 2-7$$

The first order term  $\langle \underline{k} | V | \underline{k} \rangle$  simply represents a shift in the energy levels of the electrons as can be verified by making the substitution for V(<u>r</u>) as given in 2-4. To consider the second order term in more detail

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The matrix element becomes, on using equation 2-4 for V(r)

The integral is a delta function which is non-zero only if

Thus the only contribution to the second order energy term is derived from the mixing of unperturbed states which differ by a reciprocal lattice vector. In the case where  $E_0(\underline{k}) = E_0(\underline{k} - \underline{G})$  then,

$$-\frac{h^{2}H^{2}}{2m} = -\frac{h^{2}}{2m}(h-G)^{2}$$

from which

2–10

2-11

2-8

121 = 1k - GI

Equation 2-12 defines the Brillouin zone boundary, the point at which Bragg reflection of electrons by the lattice atoms occur. The Bragg reflection gives rise to energy gaps in k space as shown in two dimensions in figure 1. The effect of the lattice on the electron wave functions is to introduce higher momentum components into the wave function;

$$\gamma_{\underline{h}} = \Sigma_{\underline{G}} \widehat{a}_{\underline{G}} e^{i(\underline{k} + \underline{G}) \cdot \underline{t}}$$

where the  $a_{G}$  are given by

$$\mathbf{a}_{G} = \frac{\boldsymbol{\zeta}_{\underline{R}} | \boldsymbol{V}(\mathbf{r}) | \underline{R} + \underline{G}}{\boldsymbol{E}_{\underline{R}}^{2} - \boldsymbol{E}_{\underline{R}}^{2} + \underline{G}}$$

It should be mentioned for completeness that higher momentum components can also contribute to the positron wave function due to the exclusion of the positron from the core regions of the solid.

The band structure of the noble metals has been found to consist of 5 narrow d bands located several electron volts below the Fermi energy which hybridize with the conduction bands. This interaction results in an extremely distorted Fermi surface (as compared with a free electron sphere) such that the surface is in contact with the <111> zone boundary. Thus one may speak of the "necks" of copper which are

2-13

2 - 14

2-12



-10-

Figure 1: Energy Gaps in k Space



Figure 2: Copper Fermi Surface

the regions of contact as shown in figure 2. The neck feature of the copper Fermi surface is used as a monitor in the study on the effects of alloying.

The nearly free electron model must be modified when applied to the noble metal alloys due to the presence of the d-bands. Pseudopotential theory has been found to be applicable to the study of some di- and tri-valent metals by Heine and Weaire (1966) and is mentioned at several points in this chapter. The following sections, which discuss the O.P.W. and A.P.W. theory, will lead to the band structure of copper.

B. Orthogonalized Plane Wave Theory

In the orthogonal plane wave (0.P.W.) treatment the conduction electron states are made orthogonal to the core electron states. The conduction electron behavior is represented by plane waves in the inter-ionic regions of the crystal and the core electrons are restricted to individual ions.

Utilizing the notation and method of Harrison (1966) an orthogonalized plane wave  $\chi_k$  is related to a core electron state  $\psi_{\alpha}$  by

$$\chi_{\underline{R}} = e^{i\underline{R}\cdot\underline{r}} - \sum_{\alpha} \gamma_{\alpha}(\underline{r}) \int \gamma_{\alpha}(\underline{r}') e^{i\underline{R}\cdot\underline{r}'} d\tau' \qquad 2-15$$

2-16

where  $d\tau$  is a volume element. The expression can be conveniently written in ket notation

$$\chi_{h} = 1h\gamma - \Sigma_{c} 1\alpha\gamma < \alpha 1h\gamma$$

-11-

which satisfies the orthogonality requirement since  $\langle \chi_{\underline{k}} | \alpha \rangle = 0$ . If the projection operator  $P = \sum_{\alpha} |\alpha \rangle \langle \alpha |$  (the operator which projects functions onto the core states) is introduced then

$$\chi_{h} = (1-P) h$$
 2-17

The conduction band states  $\psi_{\underline{k}}$  can be expanded in terms of reciprocal lattice vectors as a linear combination of O.P.W.s

If the expanded  $\psi_{\underline{k}}$  of equation 2-18 are inserted into the Schrodinger equation and all terms involving the projection operator are installed in the left hand side of the equation one can obtain

$$T\phi_{k} + W\phi_{k} : E_{k}\phi_{k}$$
 2-19

where;

pseudofunction

\$k = 26 a6(k) 18+6>

pseudopotential  $W: V(r) + \sum_{\alpha} (E_{k} - E_{\alpha}) |\alpha \rangle \langle \alpha | = V(r) + (E_{k} - H) P$ 

and the relation between the true and pseudo wave function is

$$\Psi_{k} = (1-p) \phi_{k}$$
 2-20

The net result of this analysis is the introduction of a local pseudo-potential operator given by  $(E_k - H)P$  which has the effect of

counteracting the strong attractive potential  $V_{(\mathbf{r})}$  due to the ions. In essence the conduction electron plane waves are only slightly modified in the vicinity of the ions. The application of the 0.P.W. theory to the transition metals is somewhat ambiguous since a separation of the s,p and 3d electrons into conduction and core states respectively, is not always possible. The pseudo functions however have been used with marked success by Stroud and Ehrenreich (1968) to describe the positron annihilation angular distribution spectrums of simpler metals such as aluminum and silicon.. A third method has been found to be especially useful in leading to the band structure of copper and this method is now discussed.

C. Augmented Plane Wave

A necessary requirement for any method to yield tractable solutions for the conduction electrons in a periodic potential is that the rapid convergence be obtained when the wave function is expanded in terms of the basis vectors.

The augmented plane wave method (A.P.W.) does not separate core and conduction electron states as in the O.P.W. technique but instead matches exact solutions of the Schrodinger equation for the distinct regions of k space. The potential in the A.P.W. method has two components; namely in the region about each ion core the potential is spherically symmetric (termed muffin tin) and in the region outside the core the potential is constant, figure 3. The Schrodinger equation can be solved exactly inside the muffin tin region by spherical harmonics and outside by plane waves. A brief description of the A.P.W. method as discussed by Ziman (1969) is now given.

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Figure 3: Muffin Tin Potential

The solution of the Schrodinger equation for the muffin tin region is given by

$$\Phi_{\text{IP}} : \sum C_{\text{em}} R_{\text{e}} (r \epsilon) Y_{\text{em}} (o \theta)$$
2-21

where:  $G_{m}$  expansion coefficients

Rg solution of radial equation in muffin tin region  $V_{p,m}$  spherical harmonic

The solution outside the muffin tin region is simply an expansion of plane waves

$$\chi_{\underline{R}} : \sum_{\underline{k}} c_{\underline{k}} e^{i \frac{\underline{k} \cdot \underline{r}}{2}}$$

It can be shown that the conditions imposed on the expansion coefficients  $C_{\mbox{lm}}$  by matching the solutions at the radius of the muffin tin potential are

$$C_{l,m} = (2l+1) i^{l} \left\{ \frac{\int l k R_{s}}{R_{l}(r \epsilon)} \right\} \frac{1}{\sqrt{2m}} (e^{i} \phi^{i}) \qquad 2-23$$

If the  $C_{lm}$  are placed in the expression for  $\phi(r)$  the resultant solution is termed an augmented plane wave  $\phi_k(\underline{r})$  where

$$\varphi_{k}(r): e^{i\frac{k}{k}} \varphi_{k}(r-l). \qquad 2-24$$

The l denotes the centre of the muffin tin sphere. The wave function describing the conduction electrons  $\psi_k(\underline{r})$  is a composite of the augmented

plane waves

where the  $\alpha$  expansion coefficients can be found from variational procedures.

The definitive work on the band structure of copper has been done by Burdick (1963) using the A.P.W. treatment, and Segal1 (1962) using a Green's function approach. The band structure is shown in figure 4. The bands arising from the 1s, 2s, 2p, 3s, and 3p levels of the atom lie well below the conduction band and are consequently fully occupied. The 3d band is also full and since the 3d states are localized, the band itself is quite narrow with a consequent high density of states. It has been found (Segall 1962) that the electrons in the <111> neck regions of the copper Fermi surface exhibit p-like behavior (electron density greater in the inter-ionic regions) whereas the electrons in the <100> belly regions are s-like in character (density greater at the ion sites). The two distinct characters would be expected to affect the introduction of impurity electrons into the copper system in different ways and this is discussed further in the following chapter.

The band structure calculations are completely consistent with the experimental data garnered by Halse (1969), Shoenberg (1962) and Joseph et all (1966). The most significant feature of figure 2 is that the Fermi surface has made contact with the Brillouin zone boundary in the <111> crystallographic direction resulting in the neck regions of copper. It is this particular feature of the Fermi surface which will

-16-

be used as a monitor in the study of the effects of alloying copper with different impurities.

The present chapter has attempted to provide, in a cursory manner, a theoretical basis for the behavior of the conduction electrons in copper. As well, a foundation for the study of copper alloys in the following chapter, has been laid. Some of the concepts introduced in this chapter, such as Brillouin zones, will also be referred to in succeeding chapters.

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#### CHAPTER III

#### ELECTRONS IN ALLOYS

#### A. Introduction

The eigenfunctions of the conduction electrons in pure metals are Bloch functions arising from the translational invariance of the lattice. The Bloch states have well defined energies given by

$$\mathcal{E}_{\mathbf{k}} = \frac{\hbar^2 \mathbf{k}^2}{2 \, \mathrm{m}} \qquad 3-1$$

and fill up the Fermi surface in k space. If impurity atoms are now randomly inserted into the pure metal, the concept of Bloch states becomes somewhat tenuous since the periodicity of the lattice is destroyed. The following questions pertaining to the study of these disordered alloys now arise;

- I. The validity, in a quantitative sense, of the application of the theory of pure metals to disordered alloys.
- II. If such validity does exist, the dependence of the alloy band structure on the concentration and nature of the impurity atoms.
- III. The modification of pure metal theories to conform to reality in the study of disordered alloys.
  - IV. The experimental approach to justify the relevant theories pertaining to disordered alloys.

The following discussion will attempt to answer the aforementioned questions and also to relate the role of positron annihilation to the study of disordered alloys.

#### B. Rigid Band Model

A simplistic approach in this study is to assume the only effects of alloying a solute impurity with a valence greater than that of the solvent host is to scale the Fermi energy in accord with the number of conduction electrons. This assumption is the basis of the rigid band model which also holds that the constant energy surfaces and the density of states curve remain unchanged in the disordered alloy.

Quantitative support for the rigid band model is shown in table 1 where the electron per atom ratio n at the alpha phase boundary is given for several alloys including the two studied in the present experiment. The result that the different alloys possess similar electron per atom ratios lends credence to the rigid band model as shown in figure 5 where the density of states  $N(\varepsilon)$  is plotted versus n using rigid band theory (Ziman 1960). The maximum in  $N(\varepsilon)$  occurs near n = 1.36which is the point at which a free electron sphere has expanded sufficiently to encounter the Brillouin zone boundary. The expected behavior in the density of states and also the electronic specific heat  $C_{\alpha}$  where

3-1

is to decrease once the zone boundary has been reached.

With regard to the latter prediction concerning the behavior of the density of states the rigid band model conflicts with the band structure results for copper discussed in the previous chapter. It has been found that the pure copper Fermi surface, that is n = 1, is sufficiently distorted that contact has already been made with the zone boundary.

n (∝ phase boundary)
1.384
1.408
1.406
1.360
1.420
1.270

Table 1: Electron per Atom ratios (n) for several alloys



Figure 5: Density of States versus n ( Rigid Band theory )

Furthermore, much experimental evidence has accumulated to show that for the noble metal alloys the electronic specific heat, hence the density of states, actually increases with n which contradicts the rigid band theory. Other experimental evidence (Stern 1970) also indicates failures in the rigid band theory as applied to concentrated alloy systems. Rather than totally discard the rigid band model it is worthwhile to consider some modifications of the model.

In the modified theory the eigenstate  $\phi_k$  of the rigid band model transforms to a state in the alloy system which is not an eigenstate due to the lack of periodicity in the alloy lattice. Similarly an energy transformation takes place

$$E_{(k)} \rightarrow E_{(k)} + i \left( \frac{1}{2} r(k) \right) \qquad 3-2$$

where the real part of the energy E'(k) corresponds to the true eigenstate of the alloy system and the imaginary part  $\Gamma(k)$  denotes the lifetime of the state. The eigenstate for the alloy system will be smeared out in k space where the width of the peak at half maximum is given by  $\Gamma$ . The width depends directly on the impurity concentration. The smearing of the eigenstate at the Fermi surface can, in theory, be determined by the positron annihilation method since the momentum distribution of the conduction electrons in k space is measured. In this event, the region of k space corresponding to  $k > k_f$  would indicate the sharpness of the Fermi cut-off and any smearing of the k states would be evident.

In general however, the positron annihilation technique is unable to measure the smearing of the k states except for the simplest dilute alloys such as lithium-magnesium (Stewart 1964). The reason for this is that the momentum distribution of the gamma radiation is affected by higher momentum components and also for the transition metal alloys the core states contribute an unknown amount. Both effects contribute to the smearing in k space so that any definitive conclusions are difficult to draw.

C. Tight Binding Method

Another approach has been developed by Stern (1969) for the noble metal alloys. This approach requires that the conduction bands be energetically well separated from the unfilled bands, a requirement which is met by the copper alloys studied in the present experiment.

In this method the wave functions of the alloys are Wannier functions derived from a tight binding approximation. If the wave function of the pure metal is denoted by  $\psi_{\underline{k}}(\underline{\mathbf{r}})$  and the atomic wave function for the host copper is denoted by  $\phi_1(\underline{\mathbf{r}}-\underline{\mathbf{R}}_a)$  then

$$\Psi_{\underline{k}}(\underline{r}) = \sum_{a} e^{i \underline{k} \cdot \underline{R}_{a}} \phi_{\mu}(\underline{r} - \underline{R}_{a}) \qquad 3-3$$

where the  $\underline{R}_{a}$  denote the location of the host atoms in the lattice. For the host atom copper, the conduction band will be only half filled since the band is capable of holding two electrons per atom corresponding to the two spin states of the electron.

If an impurity atom with two valence electrons is added at a lattice site s then the wave function for the alloy  $\Omega_m(\underline{r})$  can be written

-23-

$$\mathcal{N}_{m}(\mathbf{r}) = \sum_{n} a_{n}(m) \phi_{n}(\mathbf{r} - \mathbf{R}_{n})$$

where  $\phi_n = \phi_1$  for  $n \neq s$  $\phi_n = \phi_2$  for n = s

An(m) = expansion coefficients

3-4

If the two conduction electrons belonging to the impurity atom remain isolated about the atom then the impurity state  $\phi_2$  can be said to be fully occupied and additional electrons added to the system would be effectively scattered from the impurity site. The net result is that the amplitude of an additional electron state would be decreased in the vicinity of the impurity contrary to the free electron behavior which would tend to deposit additional charge at the impurity for shielding purposes. If the impurity state is not fully occupied then the scattering of conduction electrons will be s-type in nature, that is spherically symmetric. On the other hand, p-type scattering of the conduction electrons will occur if the impurity states are fully Evidence that the conduction electrons in the <100> crystaloccupied. lographic directions exhibit s-type scattering and the electrons in the <111> crystallographic neck directions display p-type behavior has been obtained (Segal1 1962).

Support for the localization of charge theory has been obtained from resistivity measurements on noble metals (Leonard 1967). These measurements indicate that the resistance of the noble metals is lower than predicted by theory (Born approximation) for scattering centres which are characterized by potentials that are localized and weak. The

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explanation in terms of charge localization is that the impurity atom states are filled and hence are not effective scattering centres for the conduction electrons.

D. Treatment of Alloy Potentials

Three methods pertaining to the study of the effective potentials seen by the conduction electrons have been applied to disordered alloy systems. These methods are now discussed briefly with no attempt to indicate their validity in terms of experimental data. It should be mentioned however, that only the most sophisticated method of the three, that is the coherent potential technique, is expected to adequately relate to concentrated alloys.

(i) Average Potential

In this treatment (Sommers 1966) the alloy potential is simply the average of the potentials of the two constituents weighted by their concentrations. The average potential at each lattice site is thus

$$V = C_1 V_1 + C_2 V_2 \qquad 3-5$$

This method has been found to be of use only for extremely dilute alloys with similar constituents and thus has very limited applicability. (ii) T Matrix

This method (Beeby 1964) is slightly more sophisticated than the average potential method. Here an average scattering matrix, the T matrix, is used where the two distinct scattered waves corresponding to interactions with the two constituents of the alloy are averaged. Thus
rather than an average potential one considers the average of the scattering properties of the two atoms. The atomic potentials chosen are usually muffin tin in nature (see A.P.W. theory in Chapter 2).

The determination of the crystal potential for either constituent is often difficult and is even more uncertain in the case of an alloy since the environment of lattice sites can vary. As well Soven (1967) concludes that the method is totally inadequate for transition metals since it introduces spurious band gaps in the energy spectrum and fails to reproduce the electronic behavior near band edges. Thus for alloys and non-simple metals this method has been superceded by a third approach.

(iii) Coherent Potential

The coherent potential model has been described by Soven (1966, 1967). It is defined as an effective potential which when placed upon the lattice sites of an alloy will reproduce the properties of that alloy. Such a potential must be energy dependent since no single potential would be expected to account for the alloy properties over a wide range of energies and in addition must be complex to provide for the damped wave functions which are characteristic of disordered alloy systems. Thus the model simulates the conduction electron behavior in an alloy by introducing a medium in which a coherent potential is placed on individual lattice sites and modifies the dynamical properties of the particle.

The coherent potential method is based on a Green's function formalism and for simplicity is discussed for a one-dimensional system. It should be noted however that the model is expected to be perfectly adequate in describing the three dimensional system (1967).

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The Green's function G(x,x') is defined for a one-dimensional alloy (Soven 1967)

$$(H_x - E) G(xx') = - \int (x - x')$$

where  $H_x$  is the Hamiltonian of the system

 $\boldsymbol{\delta}$  is the Dirac delta function.

The free electron Green's function will satisfy the initial equation with the potential set to zero

$$(-\nabla^2 - E) G_0(x x') = -\delta(x - x')$$
 3-7

and the G(xx') can be expanded in terms of the  $G_0(xx')$  in an infinite series

$$G(xx') = G_0 + G_0 \vee G_0 + G_0 \vee G_0 \vee G_0 + \cdots$$
  
3-8

where

$$G_{\bullet} \vee G_{\bullet} = \int G_{\bullet} (x,y) V_{y} G_{\bullet} (y,y) d^{3}y \qquad 3-9$$

If the crystal potential is labelled  $V_{i}(x)$  where i refers to the constituent and the  $\alpha$  to the lattice site then the total crystal potential is

 $V = \sum V_{i \propto} (\infty)$ 

3-10

3-6

Thus

$$G = G_{\circ} + \sum_{\alpha} G_{\circ} \vee i_{\alpha} G_{\circ} + \sum_{\alpha, \beta} G_{\circ} \vee i_{\alpha} (\alpha) G_{\circ} \vee i_{\beta} (\beta) G_{\circ} + \cdots$$
 3-11

The physical basis of the preceding equation is that the electrons move through the empty space of the crystal and are scattered by the atomic potentials. The scattering processes can be accounted for by the T-matrix approach discussed previously. The average scattering is given by

$$T = C_1 t_1 + C_2 t_2$$

where  $t_1$  and  $t_2$  describe the scattering for a given site and the  $c_1$  and  $c_2$  are the concentrations of the alloy constituents. The scattering matrix is related to the crystal potential V by

$$T_{i}(\alpha) = V_{i}(\alpha) + V_{i}(\alpha) G_{i} + V_{i}(\alpha) + \dots$$
 3-13

3-12

and if equations 3-11 and 3-13 are combined then

The Green's function is now described in terms of repeated scattering interactions where the electron is scattered at a specific site then moves on to another site. This expression for G is only approximate but can be readily summed. In general the model has been found to predict the position and shape of energy band edges for concentrated disordered alloys. Specifically the coherent potential model has been applied to  $\alpha$ -brass by Soven (1966) and Das and Joshi (1972) and is discussed further in a later section of the thesis.

# E. Other Methods Applicable to Disordered Alloys

# (i) Electronic Specific Heat

Since knowledge of the electronic specific heat relates directly to the density of states through equation 3-1 then a measurement of the coefficient  $\gamma$  versus the impurity concentration can be used to infer the behavior of the density of states. Much experimental evidence has been accumulated by Mizutani (1972) to show that the electronic specific heat of noble metal alloys increases with an increasing electron per atom ratio in contradiction of the theory underlying the rigid band model. It is noteworthy that this experimental evidence includes the alloy systems discussed in the present experiment.

Attempts have been made to explain these results on the enhancement of the electron-phonon interaction as the impurity concentration increases. In particular the lead alloy system (alloys of PbBi and PbT1) has been studied by Clune (1970) where the electron-phonon factor is well-known. The experimenters find that if the effects of the electron-phonon interaction are accounted for there is quantitative agreement between the increase of the specific heat coefficient  $\gamma$  and theory. A definitive check on the relevance of the electron-phonon interaction as applied to noble metal alloy systems may be garnered from a study of a superconducting transition in these alloys. Such a transition would be expected if the interaction is a rapidly increasing function of the electron per atom ratio, however copper alloys have been found to remain non-superconducting down to 0.05°K (Clune 1970).

The electron-phonon interaction is an alternative to Stern's localization hypothesis and much experimental data is needed in order to clarify the relevance of the two contributions.

(ii) Optical Measurements

Figure 6 indicates a simple picture of the band structure of copper. A narrow, filled d-band is overlapped by a wide s-band containing one electron. Two optical band transitions are shown; that from the d-band to the Fermi level and that from the Fermi level to a higher, unoccupied conduction band. A study of such transitions with a change in impurity concentrations would be expected to yield information on the band structure of the alloy. For example the rigid band model would hold that the only effects of alloying would be a shift in  $\varepsilon_{\rm f}$  to the right hence the transition from the d band to the Fermi (labelled as 1 in figure 6) level would be expected to shift to lower wavelengths and the transition from the Fermi level to the conduction band (labelled as 2 in figure 6) to shift to higher wavelengths. Such simple behavior has not been substantiated.

The prime difficulty arises since non-direct transitions are also possible whereby  $\underline{k}$  is not conserved. Unless the experimenter is able to resolve the direct and non-direct transitions then definitive conclusions are difficult. Optical spectra have been obtained for CuGa and CuGe by Biondi et al (1959) and Pells et al (1970) which relate to the changes in the copper band structure with alloying and thus are relevant to the present work.

-30-



Figure 6:

Optical Transitions in Copper

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# (iii) Inelastic Neutron Scattering

In this method the dispersion curves for phonons evinces kinks for wave numbers q corresponding to twice the Fermi surface wave vector  $\underline{k}_{f}$ . These so-called Kohn anomalies occur because the screening effect of the conduction electrons changes for the specific value of q. The screening refers to the ability of the conduction electrons to screen the periodic electric field of the lattice ions. Observation of the anomalies of  $q = 2k_{f}$  thus yields information on the shape of the Fermi surface.

Neutron diffraction studies have been done on lead by Brockhouse et al (1962) and aluminum by Stedman and Nilsson (1965). The method is predicted to be of only limited use by Shoenberg (1969) due to the weak nature of the kinks and the difficulties inherent in the method.

The Kohn anomaly can also be studied by x-ray diffuse scattering experiments. Such a technique has been applied to concentrated copper aluminum alloys by Scattergood et al. (1970).

#### CHAPTER IV

#### THE POSITRON ANNIHILATION EXPERIMENT

# A. Introduction

In this chapter several facets of positron annihilation in solids are discussed. The theoretical angular distribution of the gamma radiation, in conjunction with the different geometries, is covered in detail to provide a sufficient background for the experimental technique used in the present experiment. Other concepts such as the thermalization and lifetime of the positron and the possible enhancement of electrons in the vicinity of the positron are also included.

# B. Angular Distribution of Gamma Radiation

The methods by which the momentum distribution of conduction electrons in metals and alloys has been studied by positron annihilation relate to the particular geometry of the apertures placed in front of the detectors. As will be shown, the geometry directly affects the measurement of the angular distribution of the gamma radiation hence determines the resolution of the experiment. It should be noted that the neck of pure copper subtends an angle of about 20 degrees at the origin of k space thus the geometry used in the experiment should subtend an angle somewhat less than this.

To analyze the different geometries it is necessary to apply the conservation of momentum to the annihilation of a positron with an electron. From figure 7 one has for the transverse momentum of the gamma pair;



Figure 7: Momentum Conservation in Positron Annihilation

 $P_t = 2mc sin(\frac{\theta}{2})$ 

$$P_{l}: mc \theta: mc\left(\frac{7}{d}\right)$$

The momenta of the annihilation gamma pair is equal to the sum of the momentum of the electron and positron. As will be shown subsequently in this chapter, the positron is thermalized at room temperature hence  $P_t$  can be defined as the momentum of the electron in the transverse direction.

C. Detector Geometries

(i) Wide Slit Geometry

The wide slit geometry refers to an aperture preceding the detection system which is placed in the x-z plane such that  $l_x$  defines the length of the slit and  $l_z$  the width of the slit (figure 8'A'). A specific crystallographic direction points along the y axis and this is referred to as the axis of the system. If one of the detecting systems is translated in the z direction then specific electrons with  $P_t = P_z$ given by equation 4-2 will be counted. If  $\rho(\underline{P})$  is defined as the density of electron states in momentum space the coincidence counting rate  $N(P_z)$  will be given by the expression

4-3

4-1

4-2

-35-

The integration in the x direction is to infinity since the width of the slits is made much greater than the width corresponding to the Fermi surface radius. The integration in the y direction is also to infinity since the detectors are unable to detect the Doppler shift in energy of the annihilation radiation. If the density of electron states is assumed isotropic (Kahana 1967) and the Fermi surface spherical then

$$N(P_3) \propto g(P) \int_{\infty}^{+\infty} dP_x dP_y$$
 4-4

Since the mapping area is a disc in momentum space, figure 8'B', the integration can be carried out over the area of the disc using

$$P^{2} = P_{x}^{2} + P_{y}^{2} + P_{z}^{2} = P_{r}^{2} + P_{z}^{2}$$

$$4-5$$

4-6

In terms of the radius of the disc (in momentum units) the integral becomes

Thus for nearly spherical surfaces such as encountered in simple metals such as sodium one would expect a parabolic distribution for the number of gamma pairs with a specific z component of momentum. If the Fermi



# Figure 8B

Sampling Region for Wide Slit Geometry

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Figure 9 "B": Sampling region for Point Geometry

surface is not spherical but possesses features such as the necks previously discussed in connection with copper then the parabolic shape would be modified. In the case of copper, a discontinuity in the slope of the parabola would occur in the neck region.

It is also interesting to examine the region corresponding to the location of the Fermi surface cut-off. According to theory, no annihilation pairs should be detected past this point but experimental data includes substantial background counts. The reason for the background counts beyond the Fermi cut-off is two-fold; positrons can annihilate with the core electrons of copper and also higher momentum components can contribute to the background. At best a discontinuity in the slope of the parabola would indicate the cut-off point.

The major difficulty encountered with the wide slit geometry is that a sample in the form of a disc is taken in k space and this may not yield sufficient resolution to show the neck features of copper. It is for this reason that other methods have been developed in order to improve the resolution of the system.

(ii) Point Geometry

To provide finer resolution in k space it is necessary to reduce the limits of integration in the x direction. This is accomplished in the point geometry method, figure 9'A', which consists of circular apertures preceding the detectors; thus the mapping of the Fermi surface is done by cylinders as shown in figure 9'B'. If the diameter of the cylinder is made sufficiently small the integration in the x direction can be avoided. In this case the coincidence counting rate is given by

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$$N(P_{3}) \propto g(P) \int_{0}^{\infty} dP_{Y}$$
  
 $\propto g(P) \int_{0}^{\infty} dP_{Y}$ 

and using the relations

$$p^2 = P_2^2 + P_r^2$$
 4-8

$$pdp = Pr dPr$$
 4-9

the integral in equation 4-7 becomes;

$$N(P_{2}) \propto g(P) \int_{P_{2}}^{\infty} \frac{p \, d P}{P_{r}}$$
  

$$d g(P) \int_{P_{2}}^{\infty} \frac{d (P^{2} - P_{2}^{2})}{(P^{2} - P_{2}^{2})^{\frac{1}{2}}} \qquad 4-10$$
  

$$\propto (P_{f}^{1} - P_{2}^{2})^{\frac{f}{2}} \qquad for \quad P_{2} \leq P_{f}$$

A discontinuity in this distribution will occur when the cylinder passes through the copper neck region. Since the volume element in k space, which is mapped by the cylinder has been substantially reduced from that of the wide slit technique, the resolution will be correspondingly improved. The loss of counts encountered with this method can in part be alleviated by using stronger sources. The point geometry was used in earlier work in this laboratory where the diameter of the cylindrical aperture defined a resolution of about 1 milli-radian at the source. It was found that the resolution was barely adequate to clearly define the necks of CuZn alloys.

(iii) Crossed Slit Geometry

Another method has been developed and used to a considerable extent by Fujiwara et al (1966, 1967, 1968). In this technique a pair of crossed slits define the resolution function where the experimental resolution in the x direction (see figure 8'A') has been considerably improved over that employed in the wide slit geometry. For a given detector position the number of gamma pairs with specific transverse momentum  $P_t$  (equation 4-2) will be greatly attenuated thus statistical considerations place a limit on the width of the slits.

(iv) Present Geometry

In the present experiment the previous point geometry was altered in order to improve the experimental resolution. This alteration included the placement of a pair of slits in front of the collimating holes (see figure 9'A') such that the resolution in the direction of detector movement was narrowed by a factor of about 1.5. As is discussed subsequently the final resolution is among the sharpest in use at this time. As for the crossed slit geometry statistical considerations place a limit on the slit dimensions and financial considerations (each irradiation and delivery costs in the neighborhood of six hundred dollars) limits the number of samples studied.

## D. Thermalization of the Positron

The determination of the positron life-time in copper has been made (Kohonen 1967) and the result indicates a value of  $2 \cdot 10^{-10}$  seconds. If this time is compared with the thermalization time of the positron, about  $3 \cdot 10^{-12}$  seconds at room temperature, then the conclusion can be made that the thermalization of the positron is complete at the time of annihilation. The conduction electrons will possess energies of the order of seven electron volts thus the thermal energy of the positron, about 0.02 electron volts, will be negligible in comparison.

Several experiments have been carried out to determine the temperature effects of positron annihilation. In particular, Shand (1967) has studied the annihilation in sodium from 77°Kelvin to 600° Kelvin. The results of the Shand experiment show conclusively that the width of the angular distribution curve increases with increasing temperature. This smearing effect is analogous to increasing the resolution of the measuring apparatus (see following chapter) and indeed many experimenters include the effects of positron motion in terms of an increase in their resolution. The Shand data also indicates the positron effective mass to be almost twice the free electron mass.

### E. Enhancement

It would be expected that when a positron enters a metal there would be an increase in the conduction electron density about the positron due to Coulomb effects. This concept is termed enhancement and theoretical calculations (Kahana 1960) indicate the electron density to be an order of magnitude greater at the positron than elsewhere in the

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metal. The predicted Kahana enhancement has been found to be in excellent agreement with the measured angular distribution of sodium (Donaghy 1967). A plot of the theoretical electron density in momentum space versus k using the Kahana theory is shown in figure 10'A'. The electrons near the Fermi surface are most affected since scattering states are readily available to them.

A sketch of the electron density versus k in the absence of positrons and including the effects of electron-electron interactions is shown in figure 10'B' and indicates that the density of electrons decreases at the Fermi surface. This is due to some of the electrons accruing sufficient energies in order to occupy upper unfilled levels. The two effects tend to balance one another, indeed experimental evidence (Kahana 1967) points to little influence of the enhancement on the angular distribution of gamma radiation.

# F. Previous Studies

The first real evidence that positron annihilation could furnish details of the copper Fermi surface was provided by the early crossedslit angular correlation results of Fujiwara (1965). Subsequent work by Fujiwara and his collaborators with improved resolution have produced much of the existing data on the copper and copper alloy systems.

An alternative geometry, the point geometry, was first used by the University of British Columbia group (Williams et al 1965, 1968) to study the copper Fermi surface as a function of crystal orientation and concurrently Sueoka (1967) used the crossed slit system to perform the same type of study (the "rotating specimen" method). This latter method



Figure 10 "A": Enhancement effect on Electron Density (Stewart 1967)





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has been widely used by the Japanese workers. It should also be noted that Fujiwara and his associates pioneered the use of neutron irradiation to create positron active copper 64.

Measurements of the neck radius and <100> cut-off have been made on a sequence of copper aluminum alloys consisting of 2.6, 5.7, 10.6 and 15.1 atomic percent aluminum by Fujiwara et al (1968). Their results indicate an oscillatory behavior in the neck radius dimension as it initially increases with the 2.6% alloy, decreases for the 5.7% alloy and subsequently increases to about twice the pure copper neck radius for the two most concentrated systems. The most distinct neck features occur for the 2.6% and 10.6% concentrations and are included here. The other two alloys show little evidence for a neck. The neck radius for the 2.6% aluminum sample was determined to be 1.25 milliradians and the neck radius for the 10.6% sample was found to be 2.0 m.r. The latter alloy was found to have a <100> cut-off of 6.2 m.r. which can be compared with the present measurements.

In this lab Becker et al (1971) have determined the neck radius and <110> cut-off for  $Cu_{85} Zn_{15}$  and Becker (1970) has measured the same dimensions for a  $Cu_{90} Al_{10}$  alloy. In the former study the respective neck and <110> radii for  $Cu_{85}Zn$  were found to be 1.6 m.r. and 5.3 m.r. and in the latter study the corresponding values for  $Cu_{90} Al_{10}$  were 1.95 m.r. and 5.9 m.r. It should be mentioned that the point geometry used for these measurements employed an experimental resolution in the <110> direction which was almost twice the resolution of the present work.

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The long slit geometry has been used by Murray (1970) to measure the neck radii in the copper alloys with impurity concentrations of 2.5 and 5 atomic percent aluminum. The corresponding electron per atom ratios are 1.05 and 1.10 respectively. The measured neck radius for the lower impurity concentration is 1.45 m.r. and for the higher one the neck radius was determined to be 1.60 m.r. The authors also reported that the angular correlation data for a  $Cu_{78} Zn_{22}$  sample, electron per atom ratio of 1.22, did not indicate any distinct neck features, presumably reflecting the type of geometry employed.

Trifthauser (1969) has also studied a Cu<sub>78</sub> Zn<sub>22</sub> sample and found a neck radius of 1.50 m.r. representing a 50% increase over the pure copper value. This group also employed a long slit geometry to determine the momentum distribution.

Five copper-aluminum alloys have been studied by Thompson (1971). The concentrations of aluminum are about 2.5, 1.1, 7.5, 10, and 15 atomic percent. The respective neck radii are 1.2, 1.3, 1.5, 1.4, and 1.7 m.r. and all quoted values are approximate as taken from a graph. The plot of neck radius versus the electron per atom ratios for these alloys indicates a relatively smooth curve and is reproduced at a later point in this thesis.

Recent positron work has been done on the copper-zinc alloys and of particular relevance to the present experiment, the copper-germanium system. The former alloy study (Morinaga 1972) indicates a decrease in the neck radius for a 4.1% zinc concentration, a slight increase of about 10% in the neck radius for zinc concentrations up to 10% and then an

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abrupt increase of about 40% in the neck radius in the region of 20 - 30% zinc. The two alloys studied which are closest in impurity concentration to the CuZn systems mentioned above are those of 18.7% zinc and 23.6% zinc. The respective neck radii for these two alloys are about 1.15 m.r. and 1.3 m.r. The overall data for the study of seven alloys does not indicate that the neck radius is a monotonically increasing function of the electron-atom ratio.

A study of the two copper germanium alloys with about 3% and 9% germanium has been reported in a short note by Hasewaga (1972). His values for the neck radius of the respective alloys are 1.6 m.r. and 2.0 m.r. No other information regarding the experiment is available.

One further experiment should be mentioned although it is not concerned with concentrated alloys. Coleridge, Chollet and Templeton (1968, 1971) have studied dilute impurities (less than 0.1% concentration) in copper using the de Haas Van Alphen method and found the crosssection of the <111> neck increases at approximately 6 times the rate of change of the electron per atom ratio. Generally they observe that the copper gallium system seems to exhibit rigid band behavior whereas the copper germanium results differ markedly from the rigid band predictions. The authors note that Stern's hypothesis concerning the screening effect of the conduction electrons on the dilute impurities is supported by their data.

As well as the above work, several studies of copper-nickel alloys have been reported. These results are not included since the primary concern in the present work is the addition of extra conduction electrons to the pure copper. Table 2 summarizes the previously discussed data.

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Group	Alloy	n	Neck Radius (mr)
Fujiwara	CuA1-2.6	1.05	1.25
Murray	CuA1-2.5	1.05	1.45
Thompson	CuA1-2.5	1.05	1.20
Thompson	CuA1-5.0	1.10	1.30
Murray	CuA1-5.0	1.10	1.60
Thompson	CuA1-7.5	1.15	1.5
Thompson	CuAl-10	1.20	1.4
Becker	CuA1-10	1.20	1.95
Fujiwara	CuA1-10.6	1.21	2.0
Morinaga	CuZn-4.1	1.04	0.9
Morinaga	CuZn-5.4	1.05	1.1
Morinaga	CuZn-8.4	1.08	1.1
Morinaga	CuZn-10	1.10	1.1
Becker	CuZn-15	1.15	1.60
Morinaga	CuZn-18.7	1.19	1.2
Trifthauser	CuZn-22	1.22	1.45
Morinaga	CuZn-23.6	1.24	1.35
Morinaga	CuZn-24.6	1.25	1.45
Hasegawa	CuGe-3.0	1.09	1.60
Hasegawa	CuGe-9.0	1.27	2.0
-			

Table 2: Previous Measurements of Copper Alloy Neck Radii

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#### CHAPTER V

#### POSITRON ANNIHILATION FACILITIES

# A. Introduction

The copper alloy to be studied is placed mid-way between two systems of detectors which are separated by 16 meters (figure 11). Each system is composed of seven detectors which are aligned in pairs through the sample. The gamma detectors are preceeded by a 10 cm thick block of lead into which are drilled 6 mm diameter holes. In essence this means that the space of the sample is mapped by seven different cylinders each one slightly inclined to another (by <0.2°). One system of detectors can be varied in a sideways direction corresponding to a translation in the <110> direction.

Pulses from the aligned pairs of detectors are fed into a pre-amp discriminator and then to a coincidence box which yields an output if the incoming pulses are separated by less than 25 nano-seconds. An output pulse from the coincidence box indicates a legitimate positron annihilation event and a plot of the coincidence output versus detector position serves as the basis for the experimental results.

B. Samples Studied

The seven samples studied were either purchased from Materials Research Corporation \*\* (Cu, CuGa 4.9%, CuGa 8.7%, CuGa 12.7%, CuGe 6.0%)

All compositions refer to atomic percent concentration of impurity in copper.

Materials Research Corporation, Orangeburg, New York.



Figure 11: Block Diagram of Apparatus

or grown in the metallurgy department at the University of British Columbia (CuGe 3.3%, CuGe 8.2%). The alloys were all grown by the Bridgman method and all samples were independently analysed to determine the impurity concentration.

In all cases the bulk single crystal is cut with a spark cutter in the form of a cylinder with the axis along a <111> crystallographic direction. Since we desired to sweep the moveable set of detectors in a <110> direction (to effect the most distinct neck-belly boundary possible) it was necessary to define this direction on the sample. This was accomplished by squaring the sides corresponding to a <110> direction with a spark cutter; thus the sample would sit in the holder such that a <111> axis would point in the direction of the detectors and a <110> axis would point in the direction of detector movement.

The factors influencing the sample size include the geometry of the apparatus and the radio-activity desired. Since slits of dimensions 3.5 mm by 6 mm in the z and x directions were installed in front of the 6 mm holes for all runs the corresponding sample dimensions, on the average, were made 2.8 mm x 4.5 mm. The length of the sample was 6 mm to insure adequate statistics for a given run. After spark cutting the samples were chemically polished to remove surface residue and re-x-rayed to insure single crystal structure.

The prepared copper alloys are sent to Atomic Energy of Canada and subsequently placed in the NRU reactor (neutron flux of  $1.8 \cdot 10^{14}$  n/ cm<sup>2</sup>/sec) for a period of three days. The radiation of the normal copper 63 with neutrons yields the positron active copper 64 isotope with a half life of 12.7 hours. The radioactive sample, usually consisting of

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600 milli-curies of positron activity, is sent via Air Canada and placed in the holder. As the experiment progresses corrections must be applied for the radio-active decay. These corrections were minimized by counting at each detector position for either four or eight minutes and re-cycling the detectors back and forth about the centre axis to allow for folding of the results. The useful counting time for a sample is about one day.

#### C. Detector Arrangement

A schematic of one pair of the detecting apparatus is shown in figure 12. All but two of the gamma radiation detectors consist of sodium iodide crystals coupled to RCA 6342-A photo-multiplier tubes. The other two sodium iodide scintillators were coupled to RCA 6810 photomultiplier tubes. The detectors are encased in lead sheets to minimize the background radiation.

As previously mentioned, one system of seven detectors is variable in a direction parallel to a <110> crystallographic axis of the sample. This was accomplished by sending a start pulse from the master timer to a motor. This pulse would activate the motor which would turn a threaded axle connected to the detectors. The stop pulse occurs when a microswitch riding the rim of a disc connected to the axle reaches a groove cut in the disc. Each movement of the detectors between the start and stop pulses corresponds to an angle of about 0.2 milli-radians at the sample.

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Figure 12: Arrangement of one set of detectors

During the course of the experiment better resolution was obtained by cutting another groove in the disc opposite to the initial groove. The enhanced resolution has the drawback of poorer statistics and requires highly radioactive samples.

Since the seven sets of detectors cannot occupy the same position in real space the <111> axis of the system was located such that four sets of detectors were to one side of the axis and the other three sets to the opposite side. The maximum angle between the extreme sets of detectors and the <111> axis of the system is 1.8°. The correspondence in k space is that each mapping cylinder is slightly inclined to each other however this will have little bearing on the results since the neck of copper intercepts the origin of k space at an angle of 20°. This point is discussed further in the section on resolution.

D. Electronics

(i) Pre-amp Discriminator

The function of this circuit, figure 13, is to produce a well defined positive pulse of 1.5 volts amplitude capable of being driven through 8 meters of cable to a coincidence box. The negative pulses from the photo-multiplier tube are first inverted by the 2N964 transistor and then amplified and re-inverted by the 2N706 A transistor. The purpose of the delay line is to produce a bipolar pulse, the negative portion triggering a change in state of the bistable multivibrator. The positive portion of the bipolar pulse resets the pair to their original state. The output from the multivibrator triggers the tunnel diode which produces a positive pulse of 0.5 volts amplitude and 25 nano-seconds



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Figure 14: Coincidence Circuit

width. The final stage of the circuit is an emitter follower to match the cable impedance. The second output was used as a monitor to observe the output pulses.

The circuit acts as an energy discriminator in that gamma radiation with energy below 150 kev will not produce an output. The discrimination is necessary to insure that random noise pulses from the photomultiplier tube will not trigger the circuit.

(ii) Coincidence Box

The coincidence circuit is shown in figure 14. Initially the tunnel diode and transistors are biased off. A change in the quiescent state of these components occurs if two pulses from the discriminators of the matched detectors overlap to produce an input pulse of three volts. When the tunnel diode is triggered on, the voltage at the base of the 2N797 increases turning the transistor on. The output pulse is stretched by the 200 pf capacitor and is about 5 volts amplitude. This pulse is fed into a scaler which is controlled by a master timer.

The nominal resolving time of the coincidence box can be adjusted by varying the bias on the tunnel diode through the 10 k pot. The measurement of the resolving time can be obtained from the random source method; two uncorrelated sources are placed near the two sets of detectors and the random coincidence rate Nc measured. From the relation

$$N_{\rm C} = 2 \, \gamma \, N_1 \, N_2 \qquad 5-1$$

where  $N_1$  and  $N_2$  are the single rates, the resolving time  $\tau$  can be found. The resolving times of the seven coincidence boxes employed in the experiment ranged from 18 nano-seconds to 25 nano-seconds.

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E. Resolution Effects and Detector Considerations

The resolution of the point geometry system was determined by dividing the sample and the collimating holes into very small elements and then summing over all these elements with a computer. If all possible combinations of these elements are taken into consideration and the resultant angles noted one can plot the resolution function directly. This resolution function is described in greater detail in the following chapter.

The important consideration is the angle the resolution function subtends at the origin of k space. Designating this angle by  $\phi$  we can proceed as follows; take the ratio of the transverse momentum  $P_t$  and the momentum defined by a vector drawn from the origin of k space to the Fermi surface  $P_f$ . This ratio is equal to the sine of one-half the resolution angle  $\phi$ . The transverse momentum had already been defined (Chapter IV) and is equal to  $m_0 c\theta$ . The Fermi momentum is given by  $(2m_0 \varepsilon_f)^{1/2}$  where  $\varepsilon_f$  is the Fermi energy so

$$\sin\left(\frac{\phi}{2}\right) = \frac{m_o c \Theta}{(2m_o E_f)^2} \qquad 5-2$$

Using  $\epsilon_f = 7$  e.v. and  $\theta = 1$  milli-radian the angle  $\phi$  is equal to 13°. Since the angle subtended at the origin of k space by the necks of copper is 20° then the neck features should be defined by the apparatus.

Prior to commencing the present experiment an improvement to the resolution was made since it was known we would be dealing with impurity concentrations of sufficient magnitude (electron atom ratios of 1.25) such that the neck region might not be as distinct as for intrinsic

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copper. The improvement was made by placing lead slits preceding the 6 mm holes so that the width along the direction of detector movement became 3.5 mm. In terms of the angular resolution at the origin of k space the angle  $\phi$  is now about 7°. The resolution function is no longer cylindrical in nature but becomes a rectangular pipe mapping k space. The resolution was found to be adequate up to the highest impurity concentration studied in the present experiment.

As previously mentioned a <111> axis of the sample defines the axis of the system however since seven sets of detectors at either end are used it is impossible to position them all along the axis. Figure 12 indicates one set of detector positions; four sets of detectors (defining two vertical planes) were positioned to one side of the axis and three sets of detectors (all in the same vertical plane) were located on the other side. The distance from the <111> axis to the extreme set of detectors is 25 cms and this corresponds to an angle of 1.8°. In essence this means that the mapping surfaces are inclined to one another by <4° in the case of the extreme sets of detectors and the third set lies somewhat in-between.

It must be noted that the contribution of the positron motion has not been considered up to this point. Since the experiments are done at room temperature the positrons are thermalized and will be characterized by a momentum distribution given by Maxwell-Boltzmann statistics. Donaghy (1964) has found that the positron motion can be thought of as a contribution to the resolution function of an additional 0.05 milliradians. This contribution does not appreciably alter the calculated resolution function.

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# F. Chance Coincidence

The contribution of chance coincidence to the correlation data can be estimated using equation 5-1. If one uses an average value for the resolving time of 21 nano-seconds and average singles values of 1800 counts per second (as determined at the start of each run) then the calculated chance coincidence rate is about 8 counts per minute. An average value of coincidence counts for that period of time is  $\sim$  200 so the chance coincidence contributes about 4%. The cut-off data generally has about 80 counts per minute at the start, however since the cut-offs are not measured until the neck widths have been determined the singles rates are much lower, of the order of 1000 counts per second. In this case the chance coincidence constitutes about 3%. The corrections for this time varying contribution to the angular correlation were easily carried out.

# G. Neutron Damage

The use of neutron radiation to create the source of positrons has one major drawback in that possible damage may be done to the sample. The extent of such damage is largely unknown and most experimenters simply follow the convention of re-x-raying their sample after the neutron bombardment. No alteration in the x-ray pattern as compared with the pre-neutron bombardment pattern is considered sufficient evidence that no major damage has occurred to the sample. This method is obviously of only limited accuracy. Recent work howevery by Senicky (1973), has compared the angular correlation obtained from a neutron

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irradiated copper sample with that using a sodium 22 source for the positrons. No difference between the curves is observed for angles less than 7 m.r. however the two graphs differ for values of  $\theta$  above 8 m.r. In this experiment the largest angle studied was 6 m.r. so this recent data coupled with the x-ray analysis is considered verification that the effect of neutron bombardment on the angular distribution is small. In any event no sample in this experiment was irradiated twice - if a second run was desired then a second sample was cut.
# CHAPTER VI

# EXPERIMENTAL ANALYSIS

# A. Theoretical Resolution

The effects of the experimental resolution on the determination of the pure copper Fermi surface has been calculated by Petijevich (appendix I) for both the point geometry and the new higher resolution geometry. This computer determined resolution is found by dividing the collimating slits and the sample into small elements and calculating the number of coincidences possible between these elements as a function of angle. The resultant resolution function is closely represented by a Gaussian with a full width-half maximum (F.W.H.M.) in the z direction of 1.13 m.r. for the point geometry and a F.W.H.M. of 0.735 m.r. for the high resolution (the F.W.H.M. in the x direction for the high resolution is 1.12 m.r.). The resolution also includes an enhancement factor (Kahana 1967), however it ignores the complicated effects associated with the contribution of higher momentum components to the electron and positron wavefunctions. In addition, it should be noted that the positron mass is chosen to be equal to the free electron mass (experimental evidence indicates a positron mass in the neighborhood of twice this value), however this over-estimation in broadening is partly compensated for in that the slit width adapted for the experiment is slightly wider than used in the theoretical calculations.

The effect of folding the resolution function into the copper Fermi surface described by Roaf (1962), along with the angular distribution data for copper, are shown in figure 15. It is obvious from the figure

that relatively poor agreement is achieved and the contribution of core annihilation, principally from the d band, to the angular distribution must be considered. An indication of the difficulty involved in accounting for the core effects is apparent from the work of Senicky (1973). The Senicky calculation, using a plane wave expansion in terms of reciprocal lattice vectors (or by an alternate method using a Wigner-Seitz wavefunction) for the positron wavefunction and free atomic wave functions for the core electrons, indicate a core to conduction electron counting rate of not more than 0.1 at  $\theta = 0$  m.r. This result, which pertains to the identical orientation used in the present work, is well below the counting rate for  $\theta > \theta_f$  encountered in the copper angular distribution in figure 15 and at odds with experimental data from other positron work on copper. For the sake of comparison, we have assumed that the higher of the Senicky calculated core contributions will be unaffected by the present resolution function (since the core effects are relatively constant for  $\theta < 6$  m.r) and have arbitrarily adjusted the core to conduction ratio at 6 m.r. to be 0.25 relative to the theoretical conduction electron distribution discussed earlier. The results are shown in figure 16 and slightly better overall agreement is achieved. It is possible the inclusion of the electron higher momentum components would further improve the agreement, however the use of Kahana's enhancement factor is questionable in view of the results of Fujiwara (1966, 1968) that an abnormally large enhancement occurs in the neck region. A consistent corroboration of this has been found in the results of Morinaga (1972). On the other hand evidence for "negative enhancement" of the higher momentum components has been found by Fujiwara et al (1971). Yet

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Resolution Function folded into Copper Fermi Surface--core included

another complication may arise from the diffraction of the gamma rays (Hyodo et al 1971, Hyodo 1973) which can have significant effects upon the shape of the angular distribution curves. We can only echo the conclusion of Morinaga (1972) who states that the existence of the enhancement effect combined with the unknown core contribution greatly complicates the study of the Fermi surface and it may therefore be difficult to determine quantitatively an unknown Fermi surface. Accordingly we have adopted the empirical approach of relating distinct deviations from a smooth angular distribution curve to the neck radius and Fermi surface cut-offs.

Since the pure copper neck radius and <110> cut-off have been measured accurately (Halse 1969) then a comparison of the known values with the present data should enable us to determine the effects of our measuring apparatus on the true value. Distinct deviations from smooth behavior are characteristic of not only the pure copper data but also of the alloy results as well. The following section includes an analysis based on drawing a smooth curve through the angular distribution data and attributing the difference between the measured neck radius and <110> resolution. This method is supplemented in a later section where the pure copper data is subtracted from the alloy results.

B. Copper Analysis

The analysis of the pure copper sample will be described in detail since a common analytic procedure was used for all the alloy samples. The neck region of copper intersects the Brillouin zone boundary at right angles (Segall 1962), thus a sharp discontinuity in the angular correlation

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graph should be evident when the moveable detector system passes through the neck region. The finite resolution of the apparatus and thermal motion of the positron will introduce a smearing effect on the results. Accordingly, the location of the neck region on an angular distribution curve should be manifested in a reasonably distinct drop from a central plateau region to a smooth shoulder described by a parabolic curve. The sample is oriented such that a <lll>direction is aligned along the axis of the system (towards the detectors) and a <loo> direction is parallel to the detector motion.

Figure 17'A' is the initial sweep of the moveable detector assembly from the nominal centre position of  $\theta = 0$  milli-radians to  $\theta = 3$ milli-radians. Figure 17'B' also includes the combined results of sweeps 2 and 3 where sweep 2 is from  $\theta$  = 3 milli-radians (right hand side of <111> axis of the system) to  $\theta = -3$  milli-radians (left hand side of axis) and sweep 3 is the return pass. All results have been corrected for the radioactive decay of the sample. Both curves indicate the neck region of copper. For the right hand side of the  $\theta = 0^{\circ}$  position, sweep 1 indicates a drop off in the vicinity of 1.0 m.r. and this is verified by sweeps 2 and 3. With regard to the left hand side of the  $\theta = 0$  position, sweeps 2 and 3 indicate a discontinuity in the region about 1 m.r. indicating that the true centre of the correlation coincides with the nominal centre. In the study of the alloys all but two of the angular correlations were symmetrical about the nominal centre. The two exceptions indicated a shift of 0.1 m.r. was necessary to align the true and nominal centre; the shift presumably reflecting the placement of the sample.

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The total number of counts for both sides of the  $\theta = 0^{\circ}$  axis is shown in figure 17'C'. The data is based on an even number of sweeps for each side (that is the number of sweeps from 0 to +3 milli-radians is the same as the number of sweeps in the opposite direction) to counter the effects of possible drift in the electronics.

The results of figure 17'C' indicate clearly that the true centre of the angular distribution coincides with the nominal centre. The location of the true centre enables folding of the data whereby the number of counts in channels symmetric about the true centre are added.

The folded data are shown in figure 18. The neck radius of copper is determined to be 1.20 m.r. with an uncertainty of 0.10 m.r. This result can be compared with previous determinations of the neck radius (Halse 1969 and Lee 1969) which yielded a value of 0.99 m.r. The difference between the two numbers is attributed to the effects of the experimental resolution adding about 0.20 m.r. to the present measurement.

The data for the <110> copper cut-off is shown in figure 19. The discontinuity in the angular distribution occurs at  $5.15 \pm 0.10$  m.r. and is indicated by an arrow in figure 19. The accepted value for this cut-off from the work of both Halse and Lee is 4.98 m.r., thus the cut-off data provides strong confirmation that the effect of the experimental resolution is to add about 0.2 m.r. to the measured cut-off. This correction is applied to all neck radius, <110> cut-offs, and to the single <100> cut-off measurements for the copper alloys.

It should be noted that the <110> Brillouin zone boundary occurs at 7.1 m.r., thus the Fermi surface of pure copper falls well short of

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Figure 17:

Copper Angular Distribution Data



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this boundary in contrast to the <111> direction where contact has been made. The significant contribution of core electron states to the angular distribution is obvious in the region of  $k > k_{f}$  for figure 19.

C. Copper Alloy Analysis

(i) Smooth Curve Behavior

The analysis of the copper alloy samples follows the same format as for the pure copper sample, that is first defining the true centre of the angular distribution graph then folding the results about that centre. The apparatus is constantly cycled at periods of four or eight minutes to reduce any drift effects of the electronics. A similar correction of 0.20 m.r. is applied to the alloy data for the effects of the experimental resolution.

The following copper alloy samples have been studied: 4.9, 8.7, and 12.7% gallium and 3.3, 6.0, and 8.2% germanium. All impurity concentrations are expressed in atomic percent. Each composition has been analyzed twice and is correct to within 0.1%. Three graphs have been compiled for each sample, the determination of the neck radius from the folded angular distribution, the neck width compared with the pure copper neck width, and the <110> alloy cut-off with the corresponding pure copper value. A11 quoted errors are based on one standard deviation statistical errors so a point representing 10,000 counts is correct to  $\pm$  1%. In the graphs for the <110> cut-offs the error bars for the pure copper data have been reduced in order to facilitate the interpretation of the alloy behavior. The arrows on the graphs indicate the uncorrected neck radius or cut-off feature. The neck radius has 1% peak statistics for all samples studied with the exception of the intermediate CuGe sample which has 1.25% statistics.

The results of the direct analysis of the alloy data, corrected for the effects of experimental resolution, are shown in figures 20 to 25 for the neck radius data and in figures 26 to 31 for the <110> cutoffs. A single determination of the <100> cut-off for the CuGa 12.7% sample is shown in figure 32.

The corrected neck radii and <110> cut-offs are shown in figure 33 and 34 respectively. It is readily apparent from both figures that the CuGa Fermi surface in the neck and <110> regions is expanding more rapidly than the CuGe Fermi surface. The neck radius for the highest CuGa concentration studied is over twice that of pure copper whereas the <110> cut-off is 11% higher in the alloy than in copper. The corresponding values for CuGe relative to copper are 87% and 10% respectively. Two neck radius measurements by Hasegawa (1972) are also included in figure 33.

### (ii) Difference Curve Behavior

One of the disadvantages of the method used for determining the neck radius in the alloys is that the results tend to be highly dependent upon one or two points in the angular distribution curve, which are of course subject to statistical fluctuations. Another approach is to subtract a smooth copper curve from all the alloy results and then to require that the difference curves bear some resemblance to one another within the alloy series. This family of curves places somewhat less emphasis upon individual points although, as will be readily apparent from the data, it is also a moot point but we would expect similar features to be related.

This procedure is applied to the CuGa data in figure 35'A' and the CuGe data in figure 35'B'. Shown above the figures is the difference

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Copper and CuGa 4.9 Angular Distribution



Copper and CuGa 8.7 Angular Distribution



Copper and CuGa 12.7 Angular Distribution



Copper and CuGe 3.3 Angular Distribution



Copper and CuGe 6.0 Angular Distribution

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Copper and CuGe 8.2 Angular Distribution





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Figure 34:

<110> Cut-off Results

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Figure 35 "A" and "B" Difference Curves for CuGe (top) and CuGa (bottom)

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ALLOY	Difference Curve (m	r) Direct Analysis (m.r.
CuGa 4.9	1.44	1.46
CuGa 8.7	1.73	1.62
CuGa 12.7	2.20	2,15
CuGe 3.3	1.30	1.30
CuGe 6.0	1.53	1.47
CuGe 8.2	1.72	1.86

Table 3 Neck Radius Results - Difference Curve and Direct Analysis

\* corrected for resolution

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region sampled. The curves shown represent a fit to the data where all points are equally weighted. As expected the results indicate a similar difference behavior in the alloys for  $\theta < 1$  m.r. As the neck region is approached in the respective alloys the curves show a general rise and the grouped results do indeed resemble that of a family of curves. The error bars for the difference points are  $\pm$  10 on the scale used. It is obvious that other curves could be drawn for the difference data, however the point where the peaks begin to fall, which are taken to represent the alloy neck radii and are denoted by arrows, are not especially sensitive to weighing an individual point more or less.

The results of the analysis are tabulated (table 3) and also included are the corrected neck radius values previously determined by direct analysis. Reasonable agreement is evident for most samples, however the unknown effects of the resolution make a rigorous comparison difficult. It would be expected that the difference analysis might yield values somewhat in excess of the neck radii determined from the direct analysis, and if so the highest CuGe neck radius as found from the direct analysis may be too high. For this particular sample the quoted neck radius is taken to be an average of the direct analysis and the difference curve behavior which is found to be 1.79 m.r.

In summary, the present data has been considered from several viewpoints. The theoretical aspects of the resolution behavior on the measured angular distribution were given and found to be highly dependent on the core annihilation. This analysis is further complicated by enhancement effects and the contribution of higher momentum components. All these factors make a theoretical approach untenable. Another

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procedure, whereby a smooth curve was drawn through the data points, indicated sharp discontinuities which could be related to the neck radius and <110> cut-off. These discontinuities, when compared with the pure copper neck and <110> cut-off, indicated 0.2 m.r. should be subtracted to account for the resolution. It is this analysis, which is dependent on distinct deviations from smooth behavior in the angular distribution results that appear best suited to determine the alloy neck and cut-off features. A reasonable confirmation of these results was evident when difference curves were plotted for the various alloys. This analysis, whereby the pure copper data is subtracted from the alloy results, includes an undetermined resolution effect and yields data points with large error bars.

The present results are compared with two other alloy systems, CuAl and CuZn in figures 36 and 37 respectively. No discussion of this comparison is attempted, however it should be noted that the CuZn system is mentioned in some detail in subsequent chapters.

# D. Core Effects

It is interesting to note that an experiment of this nature might be valuable in determining the core effects due to the copper d band. If an impurity is added which will not contribute to the core annihilation (that is with a well localized d band) then the reduction in core annihilation for k <  $k_f$  correlated with the amount of impurity added would serve as an indication of the copper core contribution. If the impurity has a valence of three or four then the additional ionic charge would also tend to reduce any positron - core annihilation. It would be necessary to

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correct for higher momentum effects which, although low in the <110> direction, are expected to vary rapidly for k >  $k_f$ . To a certain extent the impurities added in the present experiment would satisfy the d band criteria although each probably accounts for a small core annihilation. Indeed the two most concentrated alloy samples for the systems studied indicate a 3% decrease in the counting rate at  $\theta = 6$ m.r., however the statistics in this region do not allow for any quantitative analysis.





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#### CHAPTER VII

#### INTERPRETATION AND CONCLUSIONS

# A. Introduction

The interpretation of the present results is made difficult due to the inherent problems in applying theory to concentrated, disordered alloys. The periodicity of the pure metal is lost in the alloying process and concepts such as Bloch states and Fermi surfaces cannot be rigorously applied to the alloy. As discussed previously, the initial approach in the alloy study, is the application of the general theory of pure metals to the concentrated alloy system. A fruitful starting point in the analysis is to assume that the alloy possesses the same electronic structure as the host, that is the additional conduction electrons occupy the k states of the pure metal. This behavior is the essence of the rigid band model and has been predicted (Stern 1969) to be of some value in describing noble metal alloys. The present chapter includes an analysis of the data in terms of rigid band predictions and also considers other implications of the experimental data.

B. Rigid Band Theory

Constant energy surfaces have been computed for copper (Faulkner 1967) using the Kohn-Korringa-Rostoker (K.K.R.) method. The potential used is essentially the same as used by Burdick who derived the copper band structure from an A.P.W. analysis. The integrated density of states  $M(\varepsilon)[M(\varepsilon_f) = n]$  has been calculated for various energies above the copper Fermi level and thus is of use in the analysis of the present

alloys. A tabulation of M( $\varepsilon$ ) versus energy (where M( $\varepsilon_f$ ) = n = 1 defines the copper Fermi level) is shown in table 4. From this table it is possible to determine the constant energy surfaces for the alloys studied in the present experiment. The Fermi energies for the alloys can be corrected for the change in the copper. lattice constant by using the results of Hume-Rothery (1936) who has studied both alloy systems. The corrected Fermi energies have been expressed in rydbergs in table 5. To evaluate the rigid band behavior of the neck and <110> cut-off it is necessary to refer to a band structure diagram for copper as shown in figure 4. The energy band structure has been expanded in the region of interest near the Fermi level in figure 38. Also shown in this figure are the <110> band and the energy band corresponding to the copper neck both of which are indicated by dashed lines above  $E_{f}$ to denote non-occupancy. The rigid band Fermi levels for n = 1.1, 1.18, 1.23, and 1.25 are drawn in increasing order above the copper Fermi level. The predicted neck radius for these n values can be found by measuring the distance from the <111> zone boundary to the corresponding intercept of the Fermi level with the <111> band. Likewise the <110> cut-offs can be found by measuring from  $\Gamma$  to the intercept of the <110> band with the appropriate Fermi surface. In both cases the predicted rigid band values are found by multiplying the measured distances by the corresponding pure copper value. The rigid band calculations are compared with the experimental data in table 6 and also in figures 39 and 40.

A similar rigid band analysis can be applied to the <100> Fermi surface using the copper band structure shown in figure 41. The predicted Fermi energy for the highest concentration CuGa alloy is shown

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E(Ry)	M(E)	E(Ry)	M(E)	+
0.66168	0.97542	0.73782	1.24141	
0.66675	0,99392	0.75475	1.29727	
0.66845	1.00002	0.77167	1.35202	
0.67014	1.00613	0.78859	1.40578	
0.67860	1.03655	0.79705	1.43261	1
0.68806	1.06673	0.80551	1.45886	
0.70398	1.12608	0.80720	1.46408	
0.72090	1.18444	0.80889	1.46932	

Table 4: Density of States in Copper for Various Energies

n	E (Rydbergs)	$\Delta E$ (Rydbergs)	
1.0	-0.192		
1.10	-0.161	.031	
1.18	-0.141	.051	
1.23	-0.131	.061	
1.25 ·	-0.124	.068	

Table 5: Rigid Band Energies for Different Electron per Atom Ratios

Alloy	Neck Radius R.B. Theory	Neck Radius Experiment	<110> cut-off R.B. Theory	<110> cut-off Experiment
CuGa4.9	1.34±.06 mr	1.46±.1 mr	5.23±.05 mr	5.10±.1 mr
CuGa8.7	1.53± "	1.62± "	5.40± "	5.41± "
CuGa12.7	1.70± "	2.15± "	5.52± "	5.59± "
CuGe3.3	1.34± "	1.30± "	5.23± "	5.10± "
CuGe6.0	1.53± "	1.47±."	5.40± "	5.35± "
CuGe8.2	1.66± "	1.79± "	5.48± "	5.48± "

Table 6: Rigid Band Prediction and Experimental Data



Figure 38: Energy Band Diagram for Neck Radius and <110> Cut-off





Neck Radius Results and Rigid Band Theory

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Figure 40:<110> Cut-off Results and Rigid Band Theory

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Energy Band Diagram for <100> Cut-off Figure 41:

and corresponds to a <100> radius of 6.20 m.r. The empirically determined <100> cut-off was found to be 5.92 m.r. after correction for the resolution. Thus the expansion of the alloy Fermi surface in this direction is less than predicted by rigid band theory. This point is discussed subsequently.

It should be mentioned that the pure copper k values used in the rigid band analysis have been taken from Halse (1969) and Lee (1969) who have calculated identical k values (correct to three figures). These values for k<100>, k<110>, and  $k_N$  are respectively 1.44, 1.29, and 0.256 in units of  $A^{\circ-1}$ . The corresponding k values in milli-radians are 5.56, 4.98, and 0.99.

The two copper alloy systems have been studied by Coleridge and Templeton (1971) in the dilute region of impurity concentration of less than 0.1 atomic percent. This group used the de Haas van Alphen method to measure the frequency of neck orbits in the alloys and, combined with previous data on the cyclotron mass (Joseph et al 1966) and thermal mass (Martin 1966), were able to calculate  $dA/d\epsilon$ . Assuming cylindrical necks, Coleridge finds that the predicted rigid behavior for the copper alloys is a neck radius versus n ratio of 3.1. Experimentally the measured ratios for the dilute CuGa and CuGe alloys were found to be 3.0 and 1.7 respectively (the extrapolated dilute alloy ratios are shown as dashed lines in figure 39). On this basis Coleridge concludes that the dilute CuGa system exhibits rigid band-like behavior whereas the CuGe alloys do not.

The present data indicates a CuGa neck radius per n ratio of 3.4 for n < 1.2. It thus appears that the addition of concentrated Ga

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impurities to pure copper has not appreciably altered the alloy neck region behavior from that of the dilute system. No measurements were made on the <100> cut-off by the Coleridge group due to the lack of sensitivity of this Fermi surface to changes in electron concentration. The discrepancy between the highest concentration neck radius (for n = 1.25) and rigid band theory is very marked and represents a true departure from a rigid band-like behavior. This point is strongly corroborated by the <100> measurement which was found to be 0.28 m.r. lower than the rigid band prediction (if the Fermi surface has bulged out in the neck region then it must be compressed in the belly region).

The present data also indicated a CuGe neck radius per n ratio of about 2.7 for n < 1.2 which is somewhat greater than the dilute measurement but still less than rigid band theory. The present data combined with the dilute CuGe work casts considerable doubt on the findings of Hasegawa (see figure 33) who quotes a neck radius of 1.6 m.r. for a CuGe alloy of n = 1.1. The Hasegawa measurement indicates a neck radius expansion well in excess of rigid band theory. His other result of a 2.0 m.r. neck radius for a CuGe alloy with n = 1.27 is consistent with the present data. The <110> CuGe cut-off results are in agreement with the neck radius data since the data points are depressed below the rigid band curve for n < 1.2. In addition, the highest concentration result does show an upward shift as noted for the neck radius behavior.

In summary, the CuGa neck radius and <110> cut-off data exhibit rigid band-like behavior for n < 1.2 and an upward departure from rigid band predictions for n = 1.25. The neck radius data extends (and agrees

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with) the observations of Coleridge for the dilute system. The neck radius departure from rigid band theory for n = 1.25 is supported by the <100> cut-off having a somewhat less than rigid band expansion.

The present CuGe neck radius data extends the dilute alloy observations of Coleridge that the neck region expansion is less than predicted by rigid band theory, although the concentrated alloys show a greater expansion than that determined for the dilute alloys. The <110> cut-off values are in substantial agreement with the neck radius data for both alloy systems presumably reflecting the pulling out of the <110> Fermi surface as the neck expands.

#### C. Alloy Fermi Surface

The neck radius, <110> cut-off and the single <100> cut-off data can be used to plot the change in Fermi surface as impurity electrons are added to the intrinsic copper. The copper crystal is a face centered cubic structure and hence the reciprocal lattice is body-centred cubic. The Brillouin zone is shown in figure 42 where the hexagonal faces of the zone are perpendicular to the <111> directions and the square faces are perpendicular to the <100> directions. The contours of the Fermi surface of pure copper can be drawn from known data on the width of the necks subtending the origin of k space and the dimensions of the <100> and <110> cut-offs relative to the Brillouin zone boundaries in those directions. The inner boundary in figure 42 represents the pure copper Fermi surface. The primary effect of adding additional electrons to the copper solvent is to increase the width of the necks as found in the present experiment. The increase in the neck dimension pulls the <110> Fermi surface outwards whereas the <100> Fermi surface expands only slightly.

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In figure 42 the three boundaries beyond the pure copper Fermi surface correspond to the copper gallium alloys studied in the present experiment. The <110> Fermi surface for the alloys appear to increase in a monotonic fashion with no evidence of bulging towards the zone boundary. The measured <100> cut-off for the highest atomic percent concentration copper gallium alloy indicates less bulging of the Fermi surface in the <100> direction as the alloy concentration increases. This result is due to the proportionately greater increase in neck radius compared to the slow increase in the <100> cut-off.

The copper germanium results (figure 43) are quite similar to the CuGa data although the neck expansion is not nearly as pronounced. No <100> Fermi surface cut-off was obtained for the CuGe system, accordingly no contours have been plotted in the belly region. On the basis of the CuGa results it would be expected that the <100> CuGe Fermi surface would tend to bulge out slightly from that of the CuGa Fermi surface. This reasoning follows from the larger CuGa neck expansion relative to CuGe as shown in figure 39.

### D. Discussion

There is no explicit theoretical calculation of the Fermi surface for the alloy systems studied. The only quantitative statements that can be made relate to the rigid band model which, in an unmodified form, is unable to account for electronic specific heat measurements. It has been suggested by Stern (1969) however, that the noble metal alloys may fortuitously exhibit a rigid band-like behavior due in part to the large energy gap between filled and unfilled conduction bands.

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Figure 42:

Copper Gallium Fermi Surface Contours



# Figure 43:

Copper Germanium Fermi Surface Contours

The present CuGa neck radius data indicates a slightly larger dependence upon the electron per atom ratio than predicted by the rigid band model for n < 1.2 and a progressively larger dependence at the highest concentration studied (n = 1.25). The latter measurement is confirmed by the less than rigid band increase in the <100> Fermi surface cut-off for that alloy. The neck radius behavior for n < 1.2 is in close agreement with the Coleridge and Templeton work (1971) on dilute CuGa alloys.

The <100> Fermi surface measurement has special significance in terms of the Hume-Rothery rules. It has been suggested by Hume-Rothery and Roaf (1961) that the reason for the  $\alpha$ - $\beta$  phase transition in the neighborhood of n = 1.40 for the noble metal alloys may be due to contact of the <100> Fermi surface with the Brillouin zone boundary. If we extrapolate the measurement for the n = 1.25 CuGa alloy, there is little likelihood of such contact at n = 1.40. A recent communication from Stern also indicates there is no contact with the boundary for gold alloys up to n = 1.42.

The positron annihilation method is not sensitive to the variation in the energy gap between the lower filled conduction band (point  $L_2$ , in figure 44) and the upper unoccupied band (point  $L_1$  in figure 44). It is clear however that relative to the pure copper band structure, the energy shifts resulting from the addition of gallium, are such that the energies of states in the <lll> neck region are lowered with respect to those in the <l00> belly region.

The CuGe neck radius data has an initial rate of increase with n which is somewhat less than rigid band and although a subsequent rise

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appears to occur for n = 1.23, the data is consistently below the CuGa results. Likewise the <110> cut-offs for CuGe are generally lower than the corresponding CuGa cut-offs for a given n. The work of Coleridge and Templeton on dilute CuGe alloys also indicates lower than rigid band behavior for the neck radius increase with n. It would be expected that the <100> Fermi surface radius for CuGe would be correspondingly larger than the CuGa radius for a given n however this has not been measured.

The problems involved in the interpretation of the experimental data are considerable. If the sytems studied were free electron like then information on the conduction band energy gaps could be used to determine the change in the [111] and [200] Fourier components of a local pseudo-potential. Unfortunately, for the case of copper, the analysis is greatly complicated by the interaction of the s,p conduction band with the d band. It is this hybridization which gives rise to the distorted pure copper Fermi surface. Even the simplest model for the situation requires a non-local pseudopotential (Taylor 1969) and then no simple relation exists between the energy gaps and the Fourier components.

Soven (1966) has applied a coherent potential model (see chapter III) to the  $\alpha$  phase CuZn system. The theory indicates that at 40% zinc (n = 1.40) the <111> energy gap (L<sub>2</sub>,  $\rightarrow$  L<sub>1</sub> in figure 44) should be about 10% lower than the value in pure copper with both L<sub>2</sub>, and especially L<sub>1</sub> predicted to decrease in energy as the concentration of zinc increases. Also the point X<sub>4</sub>, is still well above the Fermi level at n = 1.4 so that no contact with the zone boundary is predicted.

Another calculation using the coherent potential model has been applied by Das and Joshi (1972) to CuZn. This theory is applied to the

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measurements of the variation in the energy of the  $L_2$ ,  $+ L_1$  transition as determined by Biondi and Rayne (1959). Reasonable agreement between the theory and data is apparent up to the highest concentration studied which was 30% zinc. It should be noted that the Soven calculation predicts a much less  $L_2$ ,  $+ L_1$  energy decrease than does the Das and Joshi theory.

The application of the coherent potential theory of the CuZn system to CuGa or CuGe would not be of any value since the nature of the impurity would be expected to exert a large influence on the behavior of the alloy. The present measurements can, in part, be related to the results of other methods applied to concentrated copper alloys.

E. Optical Studies

The study of optical transitions is complicated by the assignment of the observed transitions to the band structure involved. The distinction between direct and non-direct transitions has also not been clearly resolved and it is expected that the proportion of non-direct transitions will increase with impurity concentration (Seib and Spicer 1969). As mentioned previously, a coherent potential calculation (Das and Joshi 1972) for GuZn in the  $\alpha$  phase shows rather good agreement with the optical transitions in the absorption spectra observed by Biondi and Rayne (1959).

More recently, Pelis and Montgomery (1970) have studied the absorption spectra of CuZn, CuGa, and CuGe in the  $\alpha$  phase. They state that the CuZn results are in general agreement with those of Biondi and Rayne (1959). The results for CuGa and CuGe seem to show a decrease in the

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energy of the  $L_2$ ,  $\rightarrow L_1$  transition with alloying but in the Ge case the structure is very broad. However optical measurements by Nilsson (1970) on CuGe indicates a sharper  $L_2$ ,  $\rightarrow L_1$  transition which moves to lower energies with alloying. Another feature in the spectra has been assigned to a d band to Fermi surface transition and the movement of this feature with concentration is consistent with a narrowing of the d band in all cases. The amount of narrowing is related to the atomic percentage of impurity rather than the electron per atom ratio since for a given n the d  $\rightarrow$  E<sub>f</sub> transition energy has increased to a greater extent in CuZn relative to CuGa or CuGe. The d bands of the solutes are in all cases much more tightly bound than in copper and as Heine (1966) has suggested a "Swiss cheese" model is appropriate for the copper d band, the holes being the solute sites. We may note that although the data is sparse, the core contribution to the annihilation rate of the highest concentration alloys studied presently is rather less than for the pure copper, presumably reflecting the fact that the solute is contributing little to the core annihilation since its d bands are tightly bound and little overlap with the positron occurs.

In conclusion, the combined optical and positron annihilation results would indicate that the effect of alloying is to decrease the <111> energy gap while at the same time shifting the point  $L_2$ , to lower energies so that a net increase in the neck radius occurs. The two effects are not entirely independent in that the present data indicates that the downward energy shift in  $L_2$ , is larger in CuGa than in CuGe and the optical data indicates the  $L_2$ ,  $\neq L_1$  shift to be larger in CuGa compared with CuGe. The energy variations with alloying depend in a complex manner on the conduction band-d band interaction and the change in lattice potential. The fact that both the energy shifts seem to be directly related to the impurity concentration rather than the electron per atom ratio is probably significant.

### F. Electronic Specific Heat Studies

For completeness the measurements of electronic specific heats in copper alloys is discussed. As previously mentioned the rigid band model predicts that the density of states for copper alloys should decrease with increasing n since the copper Fermi surface has already made contact with the Brillouin zone boundary. The measurement of the electronic specific heat  $\gamma$  can be related to the density of states N( $\epsilon$ ) by equation 3-1.

The electronic specific heat has been measured for CuZn, CuGa, and CuGe alloys (Mizutani 1972). The coefficient  $\gamma$  is found to increase with impurity concentration in all three systems suggesting that N( $\varepsilon$ ) is an increasing function of n. Thus the simple rigid band model is at odds with these measurements. One possible explanation of this behavior would be an increase in the energy gaps for all three alloy systems, however previous optical data and positron annihilation work on CuZn (Morinaga 1972) indicate the opposite change in the energy gap.

Another explanation has been offered by Stern (1970) and this is the charging concept discussed in chapter III. The density of states  $N(\varepsilon)$ is effectively increased due to the charging of conduction electrons about impurity atoms. This shielding effect at impurity sites is related to the difference in valence between the host and impurity atom and mainly affects the states near the Fermi energy. The result is an increase of  $N(\varepsilon)$  with n which is independent of the solvent band structure.

No contrary evidence to the charging concept has been presented, however it still remains to be shown that the increase in  $\gamma$  can be entirely accounted for on this basis. It has also been suggested that an increase in the electron-phonon enhancement factor may partially account for the behavior (Clune 1970).

G. Hume-Rothery Rules

As has been discussed earlier, a model for the Hume-Rothery rules was advanced by Hume-Rothery and Roaf (1961) who postulated that the  $\alpha$ phase became unstable when the Fermi surface made contact with the <200> Brillouin zone boundary. Any reasonable extrapolation of the present results for CuGa is in disagreement with this prediction. On the other hand since the CuGe results in the neck region are consistently lower than the CuGa data it is possible that contact may occur for CuGe - a measurement of the <100> cut-off for a high germanium concentration would be very desirable. Given the range of behavior observed in the neck region for the alloys studied to date: CuZn, CuAl, CuGa, and CuGe one would have to conclude that the detailed shape of the Fermi surface can only be a second order effect in determining the phase boundary.

Recently Stroud and Ashcroft (1971) have claimed that the Hume-Rothery rules are a consequence of the rapid variation of the wave-number dependent di-electric screening function in the immediate neighborhood of  $2k_f$  as a result of their pseudopotential calculations for CuZn and

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CuAl using the Lindhard dielectric function. This assumption is similar to the original theory of Hume-Rothery, however Stroud and Ashcroft claim that the shape of the Fermi surface is, in part, implicit in the use of an energy dependent pseudopotential. Further measurements on concentrated alloys should lead to accurate energy calculations which can be related to the  $\alpha \rightarrow \beta$  phase transition.

#### H. Summary

This thesis has presented data upon the Fermi surface features associated with the  $\alpha$  phase alloys copper gallium and copper germanium. Considering the problems involved in the positron annihilation technique, we feel the data are among the most clear cut yet presented, reflecting the very high resolution employed. The observed changes in the pure copper Fermi surface upon the addition of concentrated impurities leads to several conclusions.

It is possible to state that on the basis of the present work the CuGa Fermi surface will not make contact with the [200] Brillouin zone boundary in the  $\alpha$  phase region contrary to the predictions of the Hume-Rothery and Roaf model. As well the results lend support to the contention of Stern that any agreement with the rigid band model in this general class of alloys is fortuitous. The Stern hypothesis, which is supported by electronic specific heat measurements, is related to the shielding of conduction electrons about impurity atoms. In essence Stern predicts that the effects of adding the impurity atoms will be minimized by shielding so that if an impurity atom with valence greater than one is added, then since one can have only two electrons in a given

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state, the other conduction electrons will have less probability of being in proximity to the impurity. Thus the addition of large amount of impurities to the noble metal host does not radically alter the band structure and accordingly concentrated alloys still possess distinct Fermi surface features (as noted presently) and lower than expected resistance (as noted by Stern (1969)). Clearly it would be of considerable value to obtain the Fermi radii in other orientations in the systems studied to obtain a complete picture of the Fermi surface. In view of the cubic symmetry, very few additional orientations would be necessary.

The agreement of the present concentrated alloy work with previous measurements on the same dilute alloys is encouraging and demonstrates that the Fermi surface in highly concentrated systems can be effectively studied by positron annihilation. To this end it should be noted that more experimental and theoretical work is required in order to make the positron method a more precise tool in this study. Such factors as enhancement, higher momentum components and core annihilation, which complicate the analysis of these experiments, will have to be studied in greater detail. Such a study, to calculate the core annihilation contribution, has been discussed in the thesis.

At present, no detailed theoretical prediction for the copper gallium or the copper germanium systems exists, however the application of the coherent potential model to copper zinc (Das and Joshi 1972) is encouraging and should stimulate (as should the present data) similar calculations for these systems.

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#### APPENDIX

The resolution function which closely approximates that used in the present work has been calculated by Petijevich (unpublished) and is discussed in chapter VI. As mentioned in the text of the thesis, the calculation involves a division of the collimating slits and sample into small elements and finding the number of coincidences between these elements as a function of angle.

The resolution function in the direction of detector movement (z direction of figure 12) is shown by the inner curve on figure 45. The full width half maximum (F.W.H.M.) for this resolution is 0.735 milli-radians. Also shown (outer curve in figure 45) is the resolution function corresponding to the x direction of figure 12 which has a F.W.H.M. of 1.12 m.r. The resolution function in the direction of detector movement can be folded into the known copper Fermi surface with the resulting effect shown in figures 15 and 16.



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Experimental Resolution Function

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