ELECTRIC FIELD GRADIENTS IN COPPER ALLOYS

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ELECTRIC FIELD GRADIENTS IN COPPER ALLOYS

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We have measured the electric field gradients at Cu atoms which are near neighbors to the nickel impurity in a dilute CuNi alloy. The technique used in this study is zero field pure quadrupole resonance which was first demonstrated by Redfield in 1963. The measured electric field gradients for this alloy system are $4.1 \times 10^{23} \text{ cm}^{-3}$, $0.84 \times 10^{23} \text{ cm}^{-3}$, $0.46 \times 10^{23} \text{ cm}^{-3}$ and $0.146 \times 10^{23} \text{ cm}^{-3}$. These measured values are compared to the values calculated by Beal-Monod. In addition the following alloy systems were measured; CuCo, CuFe and CuV. The nuclear relaxation of these alloys were measured but no satellite structure was detected.

One of the interesting results of these measurements is the similarity of the interactions measured here to the interactions in CuZn measured by Redfield. Since nickel has an unfilled 3d shell in its electronic structure one might expect magnetic interactions in the CuNi alloy. Magnetic interactions were not found. Like the nickel alloy, the zinc alloy with copper exhibits no magnetic effects.

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I. INTRODUCTION

When two metals are alloyed many interesting changes in physical properties occur. If the concentration of one of the alloy constituents is very small in proportion to that of the other, the experimental and theoretical treatment of the properties is greatly simplified since the dilute solute-solute interactions can be ignored. This paper is concerned with one physical property, the electric field environment in the neighborhood of a dilute solution of nickel in a copper lattice (CuNi).

This thesis presents the results of measurements of the electric field gradients at copper nuclei which are near neighbors to a nickel impurity. It is part of a larger program in this laboratory to study electric and magnetic interactions of copper alloys containing transition metal impurities. Our method is the so-called field-cycling double resonance method, which had been employed earlier in this laboratory for study of aluminum based alloys. We describe the method, the substantial modifications of earlier equipment which were necessary, give the results for CuNi, and set them in context with other experiments.

In general, when a few metal atoms are substituted in a host metal lattice several effects occur. Among these effects are changes due to atomic charge excess, atomic size difference and the presence of spin

magnetic moments on the substituted atom. When an impurity is substituted into the lattice an excess charge gives rise to potential fields acting on electrons near the Fermi surface. The electrons in the conduction band then redistribute themselves to compensate for the additional charge such that an electron far away from the charge center is not affected by the charge. If the atomic size of the substituted metal is different from the host, the lattice is distorted in the vicinity of the substitute, destroying the spatial periodicity of the host lattice. An uncompensated spin magnetic moment on the solute atom produces a magnetic field which polarizes electrons near the solute resulting in a spin polarization cloud around the magnetic impurity.

A. Fermi-Thomas Approximation

The problem of determining the changes due to an excess charge in a lattice was first treated in the Thomas-Fermi^{1/} linearized model. In this treatment it is assumed that the potential is small, varies slowly with distance, that the excess charge is fully compensated within some finite volume and that the electrons in the Fermi sea are nearly free electrons. One simple picture that this model implies is the case of a solute which has one less electron than the host. This metal is placed into the host lattice and the conduction band electrons of the host pile up around the impurity giving an excess of electron density near the impurity. According to the Thomas-Fermi model the potential field due to the compensating conduction band electrons is

$$V(r) = \frac{Ze}{r} e^{-\lambda r} \quad (1.1)$$

In which Ze is the electronic charge, r is the distance from the impurity and λ is a factor giving the size of the compensation cloud. The assumption of a small and slowly varying potential is not realized for a dilute alloy, however, and thus other models must be considered.

B. Friedel Approximation

Another way of viewing the same problem is in a scattering picture. A potential field exists in the Fermi sea, and the electrons which are flowing in the conduction band are scattered by this potential field. Friedel^{2/} first treated this scattering using the familiar partial wave analysis in which each angular momentum component of the scattered conduction band electrons is treated separately and the results are then added together to get the total result. In Friedel's treatment he writes the Schrodinger equation for the radial part of the scattering wave function $\psi_{k\ell}$

$$\frac{d^2 \psi_{k\ell}}{dr^2} + \left[2(E - V(r)) - \frac{\ell(\ell+1)}{r^2} \right] \psi_{k\ell} = 0 \quad (1.2)$$

and finds the following solution in the asymptotic limit of large r

$$\psi_{k\ell} = \frac{1}{\sqrt{2\pi R}} \sin(kr + \frac{\ell\pi}{2} + \eta_\ell) P_\ell(\cos\theta) \quad (1.3)$$

in which η_ℓ is the scattering phase shift of the ℓ electrons. Integrating the excess wave function density and using Poisson's equation, the resultant potential field is

$$V(r) \propto \frac{A}{r^3} \cos(2k_F r + \phi_\ell) \quad (1.4)$$

k_F is the magnitude of the wave vector at the Fermi surface and is a function of the scattering phase shifts at the Fermi surface. This potential falls off more slowly with distance than the Thomas-Fermi potential and is oscillating over a period of $1/2k_F$ whereas the Thomas-Fermi potential decreases monotonically. Placing the further requirement that there must be a net neutrality outside of the potential field gives the following relationship between the number of electrons in excess and the scattering phase shifts:^{2/}

$$Z = \frac{2}{\pi} \sum_{\ell} (2\ell + 1) \eta_{\ell}(k_F). \quad (1.5)$$

This is the Friedel Sum Rule.

Two of the physical properties which are affected by this charge compensation are the electrical resistivity and the thermoelectric power. The presence of potential fields within the metal gives rise to an additional resistivity to that found in the pure host metal. Since the mechanism causing this additional resistivity is the scattering of conduction electrons from the impurity potential, the change in resistivity can be accounted for in terms of the scattering phase shifts from the previous section. This change in resistivity^{3/} is expressed as

$$\Delta\rho = \frac{2hc}{Ze^2 k_F} \sum_{\ell} \ell \sin^2 [\eta_{\ell-1}(k_F) - \eta_{\ell}(k_F)] \quad (1.6)$$

where c is the concentration of the impurity. Likewise the thermoelectric power is changed by the addition of a solute metal because this property is also dependant upon the motion of electrons near the Fermi surface.

C. Nuclear Magnetic Resonance Effects

In addition to these two properties are the effects of the potential field seen in various types of nuclear magnetic resonance experiments. If a nucleus has a quadrupole moment this quadrupole moment can interact with an electric field gradient to shift the position of an NMR spectral line. In a pure metal each nucleus has a nuclear magnetic moment which together with all the other nuclei and their moments produce an NMR line in the radio frequency spectrum. This NMR line has a characteristic frequency and breadth. When the pure metal is alloyed with another metal the field gradients due to the impurity shift some fraction of the nuclear resonance line so the strength of the main resonance is decreased. This fractional loss of strength is the basis of a number of experiments done by Rowland^{4/} and others referred to as wipeout experiments. The effect of the impurities is to wipeout from the main resonance those nuclear resonances from nuclei close to the impurity. In an experiment done in 1960 on copper alloys Rowland measured the intensity of the copper main line as a function of the concentration of several impurity metals such as zinc, gallium, germanium and arsenic. He found the magnitude and spatial extent of the potential fields due to the impurities to be in agreement with the calculations of Köhn and Vosko^{5/} on the Friedel potential.

Another NMR experiment is the measurement of satellite lines. If the potential field from an impurity is spherically symmetric then the effect on all nearest neighbors is the same. When there are many impurities in the host metal, the nearest neighbor to each of them is affected in the same way as all the others. Each of these nearest neighbor nuclei gives a

spectral line shifted the same distance from the main line. Since the effect is the same on so many nuclei, another line is produced with a much smaller intensity than the main line. In many instances the intensity of this satellite line is large enough to be detected using NMR techniques. An important feature of this experiment is that it allows a microscopic determination of the interaction at a known distance from the impurity center. Satellite lines might arise from any shell surrounding the impurity thus defining the interaction at several distances from the impurity. This allows us to map out the variation of the potential field with distance. Experiments such as this have been performed by Drain^{6/} on aluminum zinc, Alloul^{7/} on aluminum manganese and Lang, Boyce, Lo and Slichter^{8/} on copper nickel and copper cobalt. All of these experiments were done at high magnetic fields using continuous wave NMR techniques. High field CW NMR experiments have limited sensitivity and the results are sometimes difficult to interpret.

Another set of experiments are the zero field quadrupole resonance experiments. A number of workers have used this technique, among them; Redfield^{9/} on copper zinc, Fernelius^{10/} on aluminum zinc, Minder^{11/} on aluminum zinc and aluminum scandium as well as the study reported here on copper nickel. Performing a resonance experiment at zero applied field is advantageous because the satellite lines are not smeared by the random orientation of the powdered samples.

When nuclei in metals are in an externally applied magnetic field, they see not only the applied field but also the field due to the polarized conduction band electrons. The electrons are polarized directly by the

applied field (Pauli paramagnetism) and they may also be polarized by the induced magnetic field near a magnetic impurity. The first case applied to all metals and is seen by comparing the resonance frequencies of the same nucleus in insulator and metal crystals. This change in frequency is known as the Knight shift.^{12/} When a metal has an impurity with unfilled d shells and the impurity retains its magnetic character when dissolved in the host metal, the impurity magnetic moment induces the nearby conduction band to polarize.^{13/} This localized polarization cloud shifts the resonance frequencies of the host nuclei. Alloys of copper with magnetic impurities of the Iron group exhibit many interesting properties such as the Kondo effect, and field NMR is an ideal microscopic probe of the alloy systems. Since the satellite lines at high field are affected by charge gradients as well as local spin polarization, the interpretation of the satellite lines found in high field experiments is sometimes ambiguous. A specific determination of only the charge effects using the results of a zero field experiment is helpful in this analysis. A review of the interesting properties of magnetic impurities in alloy is given by Daybell and Steyart.^{14/}

II. THEORY OF THE EXPERIMENTAL METHOD

A. Quantum Mechanical Picture

We are concerned with a single nuclear spin near to an impurity interacting with an externally applied magnetic field, the dipole fields of nearby nuclei, the electric field gradients arising from the impurity and the electrons in the conduction band. The system is described by a Hamiltonian ^{12/}

$$\mathcal{H} = \mathcal{H}_z + \mathcal{H}_d + \mathcal{H}_q + \mathcal{H}_{en} \quad (2.1)$$

where $\mathcal{H}_z$ is the Zeeman term, $\mathcal{H}_d$ is the dipole term, $\mathcal{H}_q$ is the quadrupole interaction and $\mathcal{H}_{en}$ is the electron-nuclear spin interaction. If we consider only the first term, then the Hamiltonian is written

$$\mathcal{H}_z = -\gamma \hbar \vec{H}_0 \cdot \vec{I} \quad (2.2)$$

γ is the gyromagnetic ratio, $\hbar$ is Planck's constant, H_0 is the applied static magnetic field and I is the magnetic moment spin operator of the nucleus. Solving this for the case of copper which has a nuclear spin $I = 3/2$, gives four quantum levels equally spaced at the Zeeman energies (E_m).

$$E_m = -\gamma \hbar H_0 m; \quad m = \pm \frac{1}{2}, \pm \frac{3}{2}. \quad (2.3)$$

The dipole term in the interaction acts to broaden these four energy levels. The interaction with the electron allows the nuclear spin to

make the energy exchanges with the outside world necessary to become polarized in the presence of an external DC magnetic field. The polarization of the spins in an external field occurs when the nuclei and the electrons mutually spin flip, conserving energy by changing the electron momentum and in the process the lower energy quantum levels of the nuclear spin system become more populated. The time that it takes for the nuclear spins to polarize after a magnetic field is suddenly applied is the spin lattice relaxation time, T_1 . The electron-nucleus interaction also produces the Knight shift discussed above.

The zero field quadrupole resonance experiment is performed at zero applied field ($H_0 = 0$). The Zeeman term is zero and the quadrupole term in the Hamiltonian reads

$$\mathcal{H}_q = \frac{e^2 q Q}{4I(2I-1)} \left[3I_z^2 - I(I+1) + \frac{\eta}{2} (I_+^2 + I_-^2) \right]. \quad (2.4)$$

Where Q is the quadrupole moment of the host nuclei, the q is the z component of the field gradient tensor,

$$eq = \partial^2 V / \partial z^2 \quad (2.5)$$

and η is the asymmetry parameter

$$\eta = \frac{\partial^2 V}{\partial x^2} - \frac{\partial^2 V}{\partial y^2} / q \quad (2.6)$$

The solutions for the eigenstates of this Hamiltonian are a linear combination of the familiar spin eigenstates. The eigenvalues are given by the expression

$$\begin{aligned}
 E_m &= \frac{e^2 q Q}{4I(2I-1)} \{3m^2 - I(I+1)\} \left(1 + \frac{\eta^2}{3}\right)^{1/2} \\
 &= \frac{h\nu_Q}{6} \{3m^2 - I(I+1)\} \left(1 + \frac{\eta^2}{3}\right)^{1/2} \quad (2.7)
 \end{aligned}$$

In the case of copper ($I = 3/2$) this is two states, each of which are doubly degenerate and which are separated by an energy of $h\nu_Q \left(1 + \frac{\eta^2}{3}\right)^{1/2}$

To understand the size of these various interactions consider the case of copper in an applied DC magnetic field of 10 kilogauss. The size of the Zeeman interaction is roughly 10 Mhz. The Knight shift, due to the electron-nucleus interaction, is about 20 KHz. The width of the main resonance centered at 10 Mhz is about 10 KHz. This width is due mainly to the dipole-dipole interaction. Finally, for the case of a copper nickel alloy, the strength of the quadrupole interaction of the first neighbor is about 1 Mhz.

B. Spin Temperature Picture

In the previous section only the interaction of a single nuclear spin was discussed. In this section the treatment will be generalized to include all the nuclear spins. Here the spins will be treated as a thermal reservoir which can be heated and cooled by interacting externally with applied fields and internally with other nuclei and the conduction electrons.^{12/}

Each nuclear spin in a copper lattice interacts with all of the other spins directly via the dipole fields as well as indirectly through the conduction band electrons. In addition, each spin has the internal

degrees of freedom numerated in the previous section which are the energy levels capable of being occupied. Because of the mutual interaction of all the nuclear spins we can account for the statistical occupation probability of the spin energy levels by assuming a distribution function, in this case a Boltzmann distribution. In other words, the probability that one particular spin level is populated is given by the expression

$$P(E_m) = \frac{1}{Z} e^{-E_m / kT} \quad (2.8)$$

where $p(E_m)$ is the probability that the state at E_m is occupied, Z is the partition function

$$Z = \sum_m e^{-E_m / kT} \quad (2.9)$$

and T is the temperature at which the spins are in equilibrium. The above two equations assume the existence of a temperature equilibrium and, in the absence of any applied fields causing transitions between the nuclear spin levels, this temperature is the temperature of the medium in which the copper sample is placed.

In this experiment the copper sample is immersed in pumped liquid helium at 1.4°K. The nuclear spins are polarized by an applied magnetic field of 1500 gauss where the Zeeman splittings are about 1.5 Mhz. Multiplying the 1.5 Mhz by Planck's constant and dividing by Boltzmann's constant gives an equivalent temperature of 0.0001°K. The nuclear spin levels are separated by an energy whose temperature (0.0001°K) is much smaller than the equilibrium temperature (1.4°K). The probability that

the lowest energy state is occupied is only slightly greater than the probability that the highest energy state is occupied, for this case the probability ratio is

$$\frac{P(E_L)}{P(E_H)} = \frac{e^{-E_L/kT}}{e^{-E_H/kT}} \quad (2.10)$$

Putting the above numbers into this equation gives the probability ratio

$$\frac{P(E_L)}{P(E_H)} = e^{0.0001} \approx 1.0001 \quad (2.11)$$

So the population difference between these two states is very slight, but the important point to notice is that the occupation probability of the states of all of the nuclear spins is given by the Boltzmann distribution. The only relevant parameters in the Boltzmann distribution are the Zeeman energies of each spin and the equilibrium temperature. Once having determined the Zeeman energies by solution of the Schrodinger equation for the case of a single spin, the problem becomes the determination of the dynamics of the entire spin system. When the spin system is in thermal equilibrium, the dynamics of the entire system are given by the temperature. When the equilibrium is disturbed in some way, the spin system returns to equilibrium at a rate given by the spin lattice relaxation time, T_1 . If the spin system is a thermal reservoir described by some temperature, then the disturbance from equilibrium can be seen as a heating or cooling of the reservoir. The return to equilibrium is a heat flow through some thermal link to the liquid helium bath. The

relaxation rate expresses the thermal conductivity of the thermal link and the specific heat of the spin system. The spins can be heated directly by radiating with an RF magnetic field at the proper frequency to cause transitions between the energy levels. If the radiation is intense enough, the population of all of the levels equalizes. This is equivalent to an infinite temperature. After the radiation ceases, the spins repolarize (i.e., cool) in the time T_1 .

C. Experimental Procedure

Turning to a more detailed description of the experiment, the mechanics will be described in brief and then related to the above discussion of spin temperature.

The experiment has five steps: 1) Polarization of the nuclear spins, 2) Adiabatic demagnetization of the spins, 3) Radiation of the quadrupole spins, 4) Adiabatic remagnetization, 5) Detection of the copper resonance.

In the following discussion several terms must be defined. The Zeeman spin system is all the nuclear spins under the influence of the forces specified in the Hamiltonian (Eq. 2.4), in particular, the applied DC magnetic field. The dipole spins are all the nuclear spins which are unaffected by the addition of an impurity (i.e., nuclei far removed from any impurities) and the term dipole spins will only be used when H_0 is off. The dipole spins are also referred to as the bulk spins. The quadrupole spins are those spins affected by the addition of impurities, for instance, those nuclei in nearest neighbor relation to an impurity. As in the case of the dipole spins, the quadrupole spins will only be used when H_0 is off. These three spin systems are separate thermal reservoirs

TABLE 1

	Applied Field	Magnetization (M)	Spin Temperature ($\beta = 1/kT$)	Entropy (σ)
1	H_o	$M_o = C\beta_L H_o$	β_L	$C\beta_L^2 (H_o^2 + H_L^2)$ $= \sigma_o$
2	0	0	$\beta_D = \beta_L \frac{(H_D^2 + H_L^2)^{1/2}}{H_L}$	$C\beta_D^2 H_L^2$ $= \sigma_o$
3	0	0	$\epsilon \beta_D$	$C\epsilon^2 \beta_D^2 H_L^2$ $= \epsilon^2 \sigma_o$
4	H_o	$M = C\epsilon \beta_L H$	$\epsilon \beta_L$	$C\epsilon^2 \beta_L^2 (H_D^2 + H_L^2)$ $= \epsilon^2 \sigma_o$
5	H_o	0	0	∞

β_L = Inverse Lattice Temperature

β_D = Inverse Dipole Temperature

C = Curie Constant

H_L = Local Field

ϵ = Some Fraction ($0 \leq \epsilon \leq 1$)

Figure 1 A schematic representation of the temperature reservoirs
in the zero field quadrupole resonance experiment.

MAGNETIC FIELD CYCLING TECHNIQUE

having temperatures, specific heats and thermal links to other reservoirs and heat sources. The search field, H_{1s} , is a heat source consisting of either a single frequency or a double frequency RF magnetic field. The H_{1s} induces transitions between the levels of the pure quadrupole spins (Eq. 2.7). The lattice is a thermal reservoir having infinite heat capacity whose temperature is always the measured temperature of the sample (1.4 K).

To further clarify the procedure Table 1 and Figures 1 and 2 are included. Table 1 shows a few of the variables of the experiment. The numbers correspond to each procedural step after it has been completed. Figure 1 is a schematic representation of the thermal systems defined above. Figure 2 shows the timing of the magnetic fields H_0 , H_1 , H_{1s} and the coincidence of the resonance signal.

The experimental method:

1) The experiment begins by applying a DC magnetic field for a time long enough to allow the Zeeman spin system to come to equilibrium with the lattice ($t > T_1$). The magnetization is described by Curie's Law

$$M = C\beta H. \quad (2.12)$$

The spin temperature is 1.4 K.

2) The applied field is then adiabatically turned off. Since this process is isentropic, none of the order produced in step 1 is dissipated. When the field is off, the order is stored by the spins aligning along the dipole fields. Equating the two expressions for the entropy in the first and second rows of the table gives the dipole temperature.

3) While the H_0 is off the quadrupole spins are radiated with the H_{1s} . If this field is at the correct frequency to cause transitions between the quadrupole levels, the quadrupole spins are heated. They in turn transfer some of their additional energy to the dipole spins by mutual spin flips raising the dipole spin temperature. The increase of the dipole temperature is indicated by multiplying β_D by the fraction ϵ shown in the third row of the table.

4) The H_0 is then reapplied adiabatically. The remaining order in the dipole system is then transferred to the Zeeman system. The Zeeman spins are now at some temperature hotter than the lattice.

5) While H_0 is still changing and shortly before it reaches its ultimate value of 1500 gauss, another RF field, H_1 , is applied. The frequency of H_1 is 1.2 Mhz. When the H_0 reaches the proper value, $H_0 = \frac{\omega}{\gamma}$, the H_1 induces transitions among the energy levels of the Zeeman spins. The power absorbed by the Zeeman spin system is then measured. The size of the signal measured relates directly to the magnetization remaining after the field cycling described above. This measurement technique is known as the fast passage method. From Curie's Law it is apparent that the magnetization decrease means an increase in the spin temperature as shown in the fourth row of the table. Further, the spin temperature increase is dependant directly upon the amount of power absorbed by the quadrupole spin system and the power crossrelaxed from the quadrupole system to the dipole system while H_0 remains off. This same cycling process is repeated many times, varying the frequency of H_{1s} thus determining the energy at which the quadrupole spins absorb power.

An important facet of this cycling method is the crossrelaxation process that occurs between the quadrupole spins and the bulk dipole spins while H_0 is turned off. If there were no crossrelaxation between these two systems, there would be no way to detect the absorption of power by the quadrupole spins. The crossrelaxation process occurs when a quadrupole spin changes state simultaneously with a dipole spin. This simultaneous spin flip must conserve energy; therefore there must be a dipole spin which has the same energy as the quadrupole spin previously excited by the application of the search field. The energy distribution of the dipole spins can be seen by applying the above described field cycling experiment on a sample of pure copper. This experiment is shown in Figure 3. A single frequency H_{1s} was applied and the residual magnetization was measured. The dipole spins absorb energy directly from the search field by inducing transitions between quantum levels of the nuclear spins in the presence of the local fields. Figure 3 is a graphic representation of the distribution of energies of the dipole spins. The distance below the reference level gives the number of dipole spins at a particular frequency. This is the reservoir which not only is heated directly by the search field, but in the case of the alloy, is heated by the quadrupole spin system. Structure, in addition to the curve shown in Figure 3, is indicative of absorption by the quadrupole spins and crossrelaxation to the dipole spins. For quadrupole spins absorbing energy above about 150 Khz there are not enough dipole spins of like energy to crossrelax with the heated quadrupole spins. This difficulty was resolved by Redfield^{9/} who uses a two frequency search field rather than

Figure 3 Pure copper reference signal.

the single frequency H_{1s} . The two frequencies are centered at the frequency where the quadrupole absorption is being tested. They are separated by a frequency of 5 KHz. This technique may be compared to Hartmann and Hahn's ^{15/} pulsed search field in high field nuclear double resonance. In addition more information on the details of the crossrelaxation of these systems can be found in the work of Redfield ^{9/} Minier ^{11/} and Hebel ^{16/} the book by Goldman. ^{17/}

III. EXPERIMENTAL APPARATUS

The cryogenic equipment, the sample probe and the probe supports and connections used in this experiment have been discussed by M. N. Fernelius^{18/} in his description of a similar experiment. The remaining equipment (the transmitter, the receiver and detectors, the search signal apparatus, the timing circuits, and the H_0 field pulser) largely designed and built by the author are shown in a block diagram of the apparatus (Figure 4) and described below.

The difficult and critical task of sample preparation was performed by Dr. J. Boyce,^{19/} and the details of this sample preparation are discussed in his thesis.

A. Transmitter Section

The transmitter section of the block diagram consists of a crystal oscillator, two amplifiers, two gates, a phase shifter and an attenuator. The crystal oscillator produces a radio frequency signal for the H_1 and acts as a phase reference for the separation of the dispersion and absorption parts of the NMR signal. The crystal oscillator runs at a frequency of either 1.0 Mhz or 1.2 Mhz. The signal channel of the transmitter goes to a gate which pulses the transmitter on for only about 20 milliseconds while H_0 is rising through the fast passage resonance value. From the gate the transmitter signal goes to an attenuator which controls the power radiating the nuclear spin system during fast passage. The reference channel has a gate, a delay line phase shifter and a limiter. This reference channel is fed to the double balanced mixer for phase sensitively demodulating the resonance signal.

Figure 4 Block diagram of the electronic apparatus for this experiment.

The hybrid tee is a balanced transformer which simultaneously transmits power to the coil and picks up changes caused by resonating the spins. The tee isolates the transmitter from the receiver, thus the receiver sees only the resonance signal. Details on the function of the hybrid tee are discussed by Lo.^{20/}

B. H₀ Field Pulser

The field pulser, shown in Figure 5, is adapted from the design by Redfield, Fite and Bleich.^{21/} It is basically a programmable constant current power supply. The programming is performed by switching a reed relay between ground and a reference voltage from a mercury cell. The feedback amplifier acts to null the sum of the reference plus the voltage developed across the shunt resistor. The null condition for a grounded reference is zero field, and the null condition for the voltage reference is the high field (~ 1500 gauss). The Capacitor, C_1 , is used to absorb the power stored in the magnet coil and then slowly dissipates the power through the 10 ohm resistor until the next field cycle when the field is again turned off.

C. Search Field Apparatus

The search signal is produced by combining the signals of two oscillators in a suppressed carrier mixer. The output of the suppressed carrier mixer is only the sum and difference of the two frequencies at the input with no components of the original two frequencies. The difference frequency is maintained constant (5 or 10 KHz) and the search frequency is swept over the frequency range in interest. The suppression of the difference

Figure 5 Schematic of magnetic field cyclier.

frequency component is crucial because even a small amount of this difference frequency in the search field causes direct absorption by the dipole spins and severely limits the sensitivity of this experiment. The signal is amplified by a 100 watt power amplifier which powers a tuned circuit consisting of the search coil surrounding the sample and a tuning capacitor.

D. Timing Circuits

The timing circuits are made up of a series of Tektronics model 160 timers and waveform generators. A master clock controls the repetition rate of the experiment (1.5 - 3.0 secs) and properly sequences all the timing pulses for the experiment.

E. Receiver and Detectors

The receiver, shown in Figure 6, is adapted from a Princeton Applied Research low noise amplifier. The input and output impedances of the receiver are 50 ohms, the voltage gain is 200 and the noise figure of the receiver has been measured roughly at 5 db. The receiver operates at the carrier frequency and has a bandwidth of 500 Khz. The receiver signal is demodulated by a Hewlett Packard double balanced mixer model 10354A and the resulting audio signal is further amplified by a Princeton Applied Research model 113 amplifier. The output of the audio amplifier is grounded by a relay at all times except for a period of 20 milliseconds when the signal is present. The output of the audio amplifier is connected to the input of a PAR model CW-1 integrating boxcar and a Tektronics model 535 oscilloscope. The rise of the resonance signal triggers the oscilloscope ~~which is set on~~ internal triggering. A pulse output from the oscilloscope is used to trigger the boxcar which measures the height of

Figure 6 Schematic diagram of the low noise receiver.

the resonance signal. This complex connection of electronic components is necessitated by the time instability of the resonance signal. For optimal signal to noise ratio, the resonance signal is measured only at the peak of the signal and this configuration assures the measurement of only the peak. The boxcar reads the value of the peak many times to average the signal, and the output is given by a digital volt meter. The ultimate signal to noise ratio is about 100:1.

IV. THEORETICAL REVIEW

In this section the development and the present state of the theory of quadrupole interactions in alloys will be outlined. In addition several classes of NMR experiments and the information obtained by each type of experiment will be discussed. Examples of each class of experiment will be given, and the results of the present study will be related to the estimates of the quadrupole effect in CuNi given by Beal-Monod.^{22/}

A. Electric Field Gradients

Friedel^{2/} and his coworkers have treated the problem of the interaction of solutes in an alloy by considering the scattering of the conduction band electrons from the potential produced by the solute. Using plane waves scattering from a square well potential, Friedel derived the form of the screening potential in the asymptotic limit far from the scattering center. Friedel found that the scattering phase shifts are related to the valency difference between the solvent and the solute by requiring the additional valency to be totally screened by the conduction electrons. This relationship is the Friedel Sum Rule. It is shown, along with the screening potential, in the introductory chapter.

Langer and Vosko^{23/} calculate the shielding of a fixed charge in an electron gas using a many body perturbation approach similar to a technique developed by Gell-Mann and Brueckner. They calculate the excess density of the electron gas around the fixed charge in the asymptotic limit of large r . This density is a sinusoidal function which falls off as $1/r^3$. This result agrees with the earlier result from Friedel.

Kohn and Vosko^{5/} follow the same approach as used by Friedel with the scattering plane waves replaced by Bloch functions. Their results agree with Friedel, more explicitly they find the field gradient around the scattering center to be

$$q(r) = \alpha \frac{8\pi}{3} A(\eta_\ell) \frac{\cos(2k_F r + \varphi)}{r^3} \quad (4.1)$$

where $A(\eta_\ell)$ and $\varphi(\eta_\ell)$ are given by the following expressions.

$$A(\eta_\ell) = \frac{1}{2\pi} \left(\left\{ \sum_{\ell} (2\ell+1) [-\sin\eta_\ell \cos(\eta_\ell - \ell\pi)] \right\}^2 + \left\{ \sum_{\ell} (2\ell+1) [-\sin\eta_\ell \sin(\eta_\ell - \ell\pi)] \right\}^2 \right)^{1/2} \quad (4.2)$$

$$\varphi(\eta_\ell) = \tan^{-1} \frac{\sum_{\ell} (2\ell+1) \sin\eta_\ell \sin(\eta_\ell - \ell\pi)}{\sum_{\ell} (2\ell+1) \sin\eta_\ell \cos(\eta_\ell - \ell\pi)} \quad (4.3)$$

and α is the enhancement factor. Kohn and Vosko relate their calculations to the wipeout number measurements by Rowland. They consider in detail what the screening potential looks like around the nucleus of a neighboring copper atom. The symmetry of the screening electron near a copper nucleus must be consistent with the symmetries of the core electrons on the copper atom, so the potential must be orthogonalized to all the core electrons. This correction is α the enhancement factor. The enhancement factor is calculated by integrating a single orthogonalized plane wave over an equivalent atomic sphere. Inclusion of the Sternheimer anti-shielding factor adds about 20% to the value of α . They find for copper $\alpha = 25.6$.

There are several modifications to this basic theory. The first modification discussed will be changes in the potential gradients due to lattice deformation. Next, a more detailed calculation of the screening charge density closer to the scattering center will be discussed, and finally consideration will be given to possible changes in Kohn and Vosko's enhancement factor.

B. Lattice Deformations

The first attempt to take the lattice deformation into account is the work by Blatt.^{24/} Blatt views the lattice as an isotropic elastic continuum which undergoes a fractional volume change of $\delta v/\Omega$. Blatt argues that the volume change of this charged elastic medium alters the effective valency mismatch between the solvent and the solute and that this effect can be taken into account by replacing the valency difference in the Friedel Sum Rule by an effective valency difference given by

$$Z = Z - \frac{\delta v}{\Omega} . \quad (4.4)$$

Blatt finds better agreement with residual resistivity data using this correction.

Sagalyn, Paskin and Harrison^{25/} separate the total field gradient into two parts, one due to the valency effects and the other due to the strain field gradients. The total field gradient is then written

$$q = q_{\alpha} + q_{\lambda} \quad (4.5)$$

where the field gradients on the right of the equation are respectively the valency and strain field gradients. The first of these is calculated in the standard way from the Friedel potential and the second is calculated from the "misfitting sphere model." Sagalyn finds that the magnitudes of these two contributions are comparable and that inclusion of this correction explains Rowland's wipeout data better than the previous fit by Kohn and Vosko. Sagalyn's calculation for the total field gradient at the first neighbor in CuZn is only $3.3 \times 10^{23} \text{ cm}^{-3}$ whereas the measured value is $7.2 \times 10^{23} \text{ cm}^{-3}$.

The last example of lattice deformation calculations is in the work by Beal-Monod and Kohn.^{26/} In this paper the authors take each lattice point in a displaced position, calculate the effect of the displacement of each lattice point and add the effects together. In the asymptotic region far from the impurity they find two contributions to the field gradient, one due to the displacement of atoms close to the impurity, another due to the displacement of atoms close to the observation point. The first is similar to the continuum model of Blatt and the other is the Sagalyn correction. An interesting feature of their calculation is the high degree of anisotropy in the strain field. This anisotropy is reflected in Table 1 of their paper where they show the corrections for the three crystallographic directions [100], [111], and [110] far from the substituted atom. The ratio of the field gradients from the strain fields of the [111] direction to the [110] direction is about 700. This is for the contribution corresponding to the Blatt correction. It is interesting to note that the direction of the smallest strain effect is the direction of the nearest

neighbor in an fcc lattice (copper is fcc). In other words, this contribution of the strain fields should be negligible for the case of the quadrupole splitting of the nearest neighbor. In an appendix of their paper Beal-Mond and Kohn calculate the strain field gradients in the vicinity of a germanium impurity in a copper lattice. The corrections to the field gradients for the first and second neighbors to the germanium are respectively $0.003 \times 10^{23} \text{ cm}^{-3}$ and $0.09 \times 10^{23} \text{ cm}^{-3}$. The measured values from Jensen, Nevald and Williams^{27/} are $7.4 \times 10^{23} \text{ cm}^{-3}$ and $3.0 \times 10^{23} \text{ cm}^{-3}$, far in excess of the corrections.

C. Modifications of the Theory

Another modification of the theory is an attempt by Alfred and Van Ostenburg^{28/} to find a potential valid closer to the scattering center. As in previous calculations, they assume plane waves scattering from a square well potential. They find the excess charge density by integrating the scattered wave function over all wave vectors. In their calculation they retain the higher order terms and find an excess density

$$\delta\rho(r) = -\frac{1}{2\pi^2} \sum_{\lambda=0}^{\infty} c_{\lambda} \frac{\cos(2k_F r + \phi_{\lambda})}{r^{\lambda+3}} \quad (4.6)$$

where the C_{λ} 's are coefficients which are calculated similarly to the A coefficients defined earlier. For the case of the potential very far from the scattering center only the $\lambda=0$ term is retained and the result is the Friedel charge density. It is important to note that this too is an asymptotic result.

The enhancement factor calculated by Kohn and Vosko has a large effect on the size of the field gradient seen by a neighboring nucleus. Following the method of Kohn and Vosko, Fukai^{29/} calculated the enhancement factor for aluminum and found it to be $\alpha = 10.6$. Fukai then constructed a more complicated OPW from the simple OPW used by Kohn and Vosko plus a first order perturbation term. Using this OPW Fukai finds a corrected enhancement factor of $\alpha = 22.6$. From this result one might suspect that the calculated value of α for copper is in error. However, Beal-Monod's calculations on the quadrupole effect in CuNi using Kohn and Vosko's value for α predicts a nearest neighbor field gradient only 18% different from the measured gradient reported in this paper.

V. EXPERIMENTAL REVIEW

Several types of NMR experiments measure the potential gradients and the gradient symmetries in alloy systems. Among these are the wipeout number experiments, high field CW NMR performed on powdered samples, high field CW experiments using single crystals and zero field pure quadrupole resonance experiments. The information obtained from each of these different experiments will be discussed and examples of each type of measurement will be given.

A. Wipeout Number Experiments

Wipeout number experiments are performed by measuring the intensity of the main nuclear resonance as a function of the concentration of impurities. The conceptual picture of this experiment is sphere drawn around an impurity. Inside this sphere the quadrupole interaction is large enough to split off the resonance lines of each nucleus in the sphere from the main resonance. Outside the sphere the interaction is small enough that all these nuclei contribute to the main resonance. The wipeout number is then simply the number of nuclei included within the sphere. The main line intensity is measured for several different alloy concentrations and the intensity is plotted on a logarithmic scale as a function of concentration. The expression giving the wipeout number as a function of the impurity concentration is

$$I = I_0 (1-c)^n, \quad (5.1)$$

where I is the measured intensity, I_0 is the intensity of the main resonance of the pure host metal, n is the wipeout number and c is the fractional concentration. On a logarithmic plot the slope of the straight line is the wipeout number. When the fractional concentration is taken very low (about 100 ppm) and the sample is well annealed the curve becomes a combination of two straight lines. In this case the slope of the low concentration portion is the first order quadrupole wipeout and the slope of the high concentration region is the second order wipeout of the $\frac{1}{2} \rightarrow -\frac{1}{2}$ transition. For an example of this type of data see Tompa's ^{30/} Figure 3. In Tompa's Figure 3 he shows a plot of signal vs. concentration for a CuPd alloy. From the 2 portions of this curve Tompa finds a first order quadrupole wipeout number of 1200 and a second order quadrupole wipeout number of 33. It is important to notice that neither the first nor the second order quadrupole wipeout numbers give any information about the symmetry of the scattering potential or the details of the amplitude of the potential near the scattering center. The wipeout numbers only give the range at which the first and second order quadrupole interaction is comparable to the width of the main resonance. The range of the first order quadrupole interaction is the very far region from the impurity. For example, the first order wipeout number for CuNi is $n_1 = 1250$ which includes nuclei out to about the 30th shell or a distance greater than 4 lattice constants. The range of the second order quadrupole interaction is less than the first order. For example, the second order wipeout number of CuNi is $n_2 = 19$, a range of slightly greater than 1 lattice constant, between the 2nd and 3rd

shells. Examples of wipeout number measurements are the copper alloy experiments done by Rowland^{4/} in which he measures the second order quadrupole wipeout number in fourteen copper alloys, the measurements of Fukai and Watanabe^{29/} on aluminum alloys and the measurements of Tompa^{30/} on copper alloys.

B. High Field Experiments

Most direct measurements of satellites performed in high field are done on powdered samples. The powdered samples are necessary to permit penetration of the radio frequency fields necessary to excite nuclear transitions. The penetration depth or skin depth of an RF field at 10 Mhz is only about 10 microns. The crystalline axes of each powder particle are aligned at some random orientation with respect to the direction of the polarizing magnetic field. This random orientation produces a smearing of the satellite resonance lines making detection and interpretation more difficult. More thorough discussions of the form and details of such powder patterns are given by Rowland,^{31/} Lo,^{20/} and Lo et al.^{8/} In high field experiments the first and second order quadrupole couplings can be measured as well as the magnetic coupling. Each of these couplings can be distinguished from one another by the dependence of the splittings on H_0 . In practice first order quadrupole couplings are smeared out in the powder pattern to such an extent that they are either very difficult or impossible to detect. In the case of CuNi only the second order shift of the first neighbor is seen and there is no information on the interaction at sites further from the impurity. The form of the powder pattern in a high field

experiment gives the electric field gradient q , and the asymmetry of the field gradient η , but the identification of the neighbor responsible for the splitting cannot be determined unambiguously. Examples of this type of experiment include the published alloy measurements performed in this laboratory on CuNi, and CuCo^{8/} as well as other copper alloys with transition elements yet to be published. Other examples are the measurements made by Drain^{32/} and Alloul^{7/} on aluminum alloys. The results of the experiments by Drain, Alloul and others are shown in Tables 2 and 3. The tables show the measured values of the field gradient and the asymmetry parameter for the first neighbors in dilute alloys. These tables include high field NMR, single crystal NMR and zero field NMR data.

C. Single Crystal Experiments

With the recent development of technologies permitting more sensitive NMR measurements several experimenters have measured quadrupole splittings in single crystal alloys. Among the workers making these types of measurements are Schnackenburg and Schumacher^{33/} on CuZn, Jensen, Nevald and Williams^{27/} on copper alloys, Jorgensen, Nevald and Williams^{34/} on aluminum alloys and Stakelon^{35/} on copper alloys with transition metals. These are shown in Tables 2 and 3. The advantage of single crystal measurements is that they allow the determination of not only the q and the asymmetry parameter η , but also unambiguously identify the position of the interaction. For satellite lines which can be readily detected single crystal NMR provides the most complete data available on the interactions. However relatively low sensitivity because of poor RF field penetration of the crystal is the major difficulty with this technique.

TABLE 2

Copper AlloysList of Measured Cu Alloys Giving v_Q (in Khz) and η

Co ^c 376 .44	Ni 1120 .20	Cu HOST	Zn ^b 1960 .265	Ga	Ge ^a 1940 .905	As
		Ag ^b 570 .75	Cd ^b 1520 .036	In ^a 2220 .32	Sn ^a 2300 .64	Sb ^a 2600 .75
		Av ^b 2650 .05				

^a Jensen Nevald and Williams^b Schumacher and Schnackenburg^c Thomas Stakelon

TABLE 3

Aluminum AlloysList of Measured Alluminum Alloys Giving ν_Q (in Khz) and η

Mg 152 ^a .03 152 ^b .05											Al HOST	
	Sc 630 ^c ~0	Ti	V	Cr 505 ^c .30	Mn 372 ^c .32 360 ^d	Fe	Co	Ni	Cu 121 ^b .06	Zn 148 ^c .35	Ga ^a 175 .01 174 ^b .017	Ge 246 ^a .03 250 ^b .053
									Ag 176 ^c .34 170 ^b .31			

^a Ref. 32^b Ref. 30^c Refs. 11, 34, 35

D. Zero Field Quadrupole Experiments

In 1963, Redfield^{9/} developed a technique for measuring quadrupole couplings directly. This is the zero field method described earlier and the method used in the measurements presented in this paper. The advantage of this measurement is its high sensitivity. The experiment is performed at zero applied field so there is no powder pattern to decrease the sensitivity, but since a powder is used there is no skin depth problem limiting the number of nuclei seen. Experimental results quoted are the quantity ν_Q , but unfortunately there is some confusion in the literature in its definition. The generally accepted usage is the following,

$$\nu_Q = 3e^2qQ/2I(2I - 1)h . \quad (5.2)$$

This definition is followed in the present work. The quantity ν_Q is then simply the field gradient in frequency units. Jensen et al. define ν_Q to include the asymmetry parameter η , but quote their results in units of $e^2qQ/2h$ which is the above definition of ν_Q for $I = 3/2$. The frequency measured in this thesis includes both the ν_Q and the asymmetry parameter,

$$\nu_{\text{meas.}} = \nu_Q \left(1 + \frac{\eta^2}{3}\right)^{1/2} . \quad (5.3)$$

The zero field experiment does not measure magnetic interactions. Because of the high sensitivity of the zero field method it can be used in conjunction with the single crystal measurements to first find the quadrupole satellites allowing the single crystal experimenter to concentrate his search for the single crystal satellites in a very limited region. In

addition to Redfield's original measurements in CuZn and CuAg, Fernelius^{10/} and Minier^{37/} made zero field measurements on aluminum alloys, and more recently Berthier and Minier^{38/} duplicated the measurements reported here in CuNi. Berthier and Minier indicated their measurements agree with those to be presented here.

VI. EXPERIMENTAL RESULTS AND DISCUSSION

A. Experimental Data

The quadrupole satellites measured in this thesis are shown in Table 4. Quadrupole satellites in copper generally appear in pairs, one for each isotope Cu^{63} and Cu^{65} . The lowest frequency absorption centered around 40 KHz is shown in Figure 7. Figure 8 shows the two pairs of absorptions at 225,208 KHz and 126,108 KHz, and Figure 9 shows the highest frequency pair at 1.125, 1.042 Mhz. The data in the last two figures were taken while radiating with two frequencies: the carrier indicated on the abscissa and the modulation frequency 5 KHz. The 40 KHz line was detected using a single frequency search radiation. The CuNi sample used had a nickel concentration of 0.1 at %. The sample was an annealed powder.

Table 5 is a summary of all the measurements performed for this study. In addition to the nickel alloy, cobalt, iron and vanadium and pure copper were measured. For the cobalt, iron and vanadium samples no quadrupole resonance lines were detected searching up to 2 Mhz. The spin lattice relaxation times (T_1) were measured for all of these alloy systems and in addition for annealed and unannealed pure copper. One possible explanation for the lack of results in the cobalt, iron and vanadium alloys is the radio relaxation of the quadrupole spin system to the lattice due to the effects of the spin magnetic moments on the impurities. High field experiments in this laboratory imply there may be a fast T_1 for neighbors near iron and thus other impurities in copper. Referring back to Figure 1; an increase in the relaxation rate between the quadrupole spin system and the lattice implies that the power pumped into the quadrupole spins during the search irradiation can be transferred directly to the lattice and thus

TABLE 4

SHELL	Calculated Quadrupole Resonances (Beal-Monod)		Measured Quadrupole Resonances	
	$q(10^{23} \text{ cm}^{-3})$	ν_Q (kHz)	$q(10^{23} \text{ cm}^{-3})$	ν_Q (kHz)
1	5.0	1,370 1,285	4.1	1,125 1,040
2	1.88	504 472		
3	0.56	156 146	0.84	225 218
4	0.41	114 107	0.46	125 116
5,6,7			0.146	40

TABLE 5

Table of Measurements

Copper Alloys

<u>Impurity</u>	<u>Concentration(a/o)</u>	<u>Annealed</u>	<u>T₁ (msec)</u>	<u>Satellites found</u>
Ni	0.1	Yes	365	Yes
Co	0.3	Yes	300	No
Co	0.3	No	40	No
Co	0.05	Yes	380	No
Fe	0.05	Yes	370	No
V	0.19	No	240	No
Pure Cu		Yes	400	
Pure Cu		No	400	

Figure 7 Quadrupole resonance line at 40 Khz for CuNi.

Figure 8 Quadrupole resonances at 116 Khz, 126 Khz, 218 Khz
and 225 Khz for CuNi.

Figure 9 Quadrupole resonances at 1.040 Mhz and 1.125 Mhz
for CuNi.

not raise the temperature of the dipole spin system. If the temperature of the dipole spins remains constant there is no way for this experiment to detect absorption by the quadrupole spins. Such a mechanism is supported by the measurements of Lumpkin on a CuMn powder. Lumpkin^{39/} found that the addition of 10 ppm manganese in copper increased the relaxation rate over pure copper by roughly a factor of two. Furthermore, the measurements performed on CuNi indicate some crossrelaxation bottleneck between the quadrupole spins and the dipole spins so that any competing relaxation process decreases the sensitivity of this experiment.

B. Discussion and Comparison of the Data

There are two internal consistency conditions met by the CuNi data presented. First, the ratio of the satellite pairs must be the same ratio as the measured nuclear quadrupole moments. Second, the relative absorption of the pairs must be in proportion to their isotopic abundance. These conditions are satisfied by all resolved pairs.

Beal-Monod^{22/} calculates the electric field gradients for the first four neighbors in a CuNi alloy. The EFG's are calculated from Equation (4.1). The three phase shifts s, p , and d are found using the Blatt modified Friedel Sum Rule, the experimental values for the residual resistivity (Equation (1.6)) and the experimental second order wipeout number for CuNi. The A coefficient and the phase ϕ are calculated from the phase shifts and these values are used in Equation (4.1) to find the quadrupole interactions. The values of the field gradient found by Beal-Monod for the first four neighbors are shown in Table 4. These calculated frequencies are to be compared to the measured satellite frequencies. The only previous measurement of the

quadrupole interaction in CuNi is the high field powder measurement by Lo et al.^{8/} in which they found the first neighbor coupling to be 1.1 ± 1 Mhz. It is clear that the 1.125 Mhz measurement from this work is the first neighbor interaction and the number to be compared with the calculated value of 1.37 Mhz. The agreement of the measured and the calculated couplings is good and in light of the approximate nature of the calculation (i.e., using second order wipeout numbers) is probably fortuitous. Further comparison of these data can be made to Beal-Monod's numbers and this is shown in Table 4. If the second neighbor was not seen in this experiment (there are only 6 nuclei in this shell) then the third neighbor measured is 225 Khz and the fourth neighbor is 126 Khz. These assignments are purely speculative and cannot be confirmed by these experimental data.

C. Summary and Conclusions

The data presented in this paper confirm the results and interpretation of the high field experiment on CuNi by Lo et al.^{8/} The first CW NMR data were taken by Lo using a conventional electromagnet at a field of 10 Kgauss. The data consist of number of satellite lines which could be interpreted in two different ways. Subsequent satellite studies by Lang at much higher magnetic fields (using a superconducting magnet) supported one of the interpretations. Lo detected five satellite lines which he interpreted as the peaks in the powder pattern of two second order quadrupole shifted shells. However, Lang found that only three of these peaks are due to a second order quadrupole shift and this set of satellites corresponds to the first shell with an electric field gradient and asymmetry parameter as shown in Table 2. The source of the remaining two satellites is unclear.

The resonance line found in this study corresponds to the first neighbor identified by Lang and the absence of a quadrupole resonance near 800 Khz is counter to the first interpretation by Lo.

The data presented here are the first pure quadrupole resonance results on a copper alloy with a transition metal impurity. The comparison of the results of this study on CuNi with the earlier results of Redfield^{9/} on CuZn are very interesting. The difference in the electronic structure of nickel and zinc is that nickel lacks one electron in the 3d shell and zinc has a filled 3d shell and an additional electron in the 4p shell. The unfilled d shells that characterize the transition metals produce either paramagnetic or ferromagnetic behavior in the pure transition metals. One of the interesting questions about the properties of dilute alloys of the transition metals is whether they retain their magnetic properties in solution with copper. Zinc has no magnetic character and in solution with copper produces an electric quadrupole resonance at 1960 Khz at the first neighbor. Likewise nickel also has no magnetic properties with copper and the nickel atom produces a first neighbor quadrupole resonance at 1125 Khz. The asymmetry parameters of the nearest neighbor gradients of these two alloy systems are also very similar, for CuZn $\eta = 0.265$ and for CuNi $\eta = 0.20$. From these data we conclude that the microscopic effects of alloying nickel with copper are nearly the same as alloying zinc with copper.

Probably the greatest theoretical shortcoming in the treatment of the nonmagnetic properties of dilute alloys is the failure to account for the measured asymmetry in the field gradients. The field gradients in both the Friedel approximation and the Alfred and Van Ostenburg approximation are dependant only on the radial distance to the impurity so the field gradients are axially symmetric ($\eta=0$). The above theories imply further that the field gradient at the first neighbor should scale with the valence difference between the host and the solute. Referring to the field gradients and asymmetry parameters shown in Table 2 we see that copper alloys with cadmium, indium, tin and antimony do not agree with this implication. The field gradients are nearly constant and the asymmetry parameters roughly scale with the valence difference.

There are several possible explanations of these non zero asymmetry parameters. First, there is the displacement of the neighbors of the impurity from their perfect cubic lattice positions. From the discussion of the results of the calculation by Beal-Monod and Kohn it is clear that this mechanism could result in asymmetric field gradients. A second source of asymmetry is a change of the effective charge on each lattice site. If the screening charge is not confined to the impurity, the various neighboring atoms possess a net charge which gives rise to a non zero η . The third source of asymmetry is the splitting of the d bands of the impurity by the crystal potential of the host metal. Callaway and Edwards^{40/} calculate the splitting of the d bands in pure copper and find the E_g and the T_{2g} levels split by 0.87 ev. The photoemission data of Berglund and Spicer^{41/}

indicate two bumps in the d band density of states separated by 0.9 ev. Yafet^{42/} calculates the splitting of the d states of a nickel atom in a copper matrix and finds a separation of 0.04 ev. If the nickel d bands were split this might imply a different spatial variation for the E_g and the T_{2g} scattering resonances. The resultant charge density would be reflected in an asymmetry in the field gradients. Except for the rough calculations by Beal-Monod and Kohn none of these mechanisms has been worked out to see how much it might contribute to the measured asymmetry of the alloys in Tables 2 and 3.

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He attended the University of Southern California as an undergraduate where he held a NASA research assistantship in physics during the years 1963-1966. He graduated cum laude in June 1966 and was elected to the Society of Sigma Xi. He remained at USC for another year as an NSF fellow to earn a Master of Science degree.

He began his graduate studies at the University of Illinois in September 1967. He has held an AEC research assistantship since entering the University of Illinois.