

## Pure Nuclear Electric Quadrupole Resonance in Impure Copper

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The quadrupole interaction of copper nuclei which are near neighbors of Ag and Zn impurities in metallic copper has been measured by means of pure quadrupole resonance, using the field cycling method of Ramsey and Pound in which resonance is detected by subsequent remagnetization and Zeeman resonance of spins far from the impurities. Coupling between spin systems is enhanced by applying two frequencies simultaneously separated by 20 kc/sec; this is a variant of the phase-reversal method of Hartmann and Hahn. For Ag solute, resonances are observed (due to  $\text{Cu}^{63}$ ) at 620, 475, 200, and 75 kc/sec, due to first, second, third, and fourth or fifth neighbors, respectively. For Zn a search up to 5 Mc/sec shows resolved resonances only at 1980 and 100 kc/sec which are tentatively ascribed to second and third neighbors; this assignment is based in part on Rowland's earlier data. The anomalously large interaction of near neighbors of Zn is ascribed to virtual excitation of  $d$  electrons to above the Fermi level by the impurity perturbation.

### I. INTRODUCTION

WHEN impurities are added to copper, the surroundings of copper nuclei near these impurities do not have the cubic symmetry which they do in pure copper, as a result there exists at such copper sites an electric field gradient which interacts with the nuclear quadrupole moment.<sup>1</sup> A fairly good idea of the size of these interactions can be obtained by measuring the decrease in intensity of the magnetic resonance absorption as a function of impurity content. By carefully studying the effect of many different impurities in copper, Rowland<sup>2</sup> was able to show that there is a contribution to the quadrupole interaction due to lattice strain, probably due to deformation of the copper ionic core, and a larger interaction proportional to the valence difference between copper and the added impurity. This latter interaction has been explained as caused by scattering of electrons near the Fermi surface by the impurity.<sup>3-5</sup>

In the present research we are concerned with this same quadrupole interaction, and we present some measurements of the quadrupole resonance frequency of some near neighbors of silver and zinc impurities in copper, measured directly by means of a form of pure quadrupole resonance in zero applied dc magnetic field. Nuclear resonance in metals is generally performed on powders to permit rf field penetration,<sup>6</sup> and thus it is necessary to work in zero magnetic field to avoid smearing of the resonance due to the dependence of the resonance frequency of an individual spin on crystalline orientation relative to an applied field. In zero field the

resonance frequency of a given nucleus near an impurity is nearly the same as that of every other nucleus which is the same distance from the impurity, provided that the concentration of impurities is low enough that interaction with more distant impurities is negligible.

The fact that a low concentration of impurities is required makes straightforward pure quadrupole absorption spectroscopy difficult (though it is probably possible). Instead we used a magnetic field cycling form of double resonance spectroscopy which was proposed by Ramsey and Pound<sup>7</sup> and applied to metals by Anderson.<sup>8</sup> In this technique the spins are polarized in a field of about 5000 G at a conveniently low temperature (1.3°K); the field is then turned off for a time not much longer than the zero-field spin-lattice relaxation time, and a search frequency ( $\omega_s$ ) magnetic field, of frequency  $\omega_s$ , is applied to the sample; then the  $\omega_s$  is turned off and the dc field is turned on adiabatically to 1000 G, and a sweep through magnetic resonance is made as rapidly as possible to ascertain what effect, if any, the  $\omega_s$  field had on the spin system. The naive expectation is that if  $\omega_s$  coincides with the quadrupole resonance frequency of a set of spins near impurities, the energy absorbed by these spins will be transmitted at least partially to the spin system in general,<sup>9</sup> and affect its subsequent resonance signal. Thus,  $\omega_s$  is slowly varied while the set of steps above is repeated many times; when  $\omega_s$  equals a pure quadrupole resonance frequency, the observed resonance signal decreases.

The technique described above works well at low frequencies ( $\omega_s < 150$  kc/sec), and a few well-defined resonances were found at these frequencies. However, it was expected theoretically and found experimentally that higher frequency resonances were not detectable by this technique, even using  $\omega_s$  amplitudes of several gauss. To find these higher frequency resonances, we applied two frequencies simultaneously at frequencies  $\omega_s + \Delta$  and  $\omega_s - \Delta$ , varying  $\omega_s$  and keeping  $\Delta$  roughly constant and roughly equal to the magnetic resonance

<sup>1</sup> N. Bloembergen and T. J. Rowland, *Acta Met.* **1**, 731 (1953); for a review of early work see M. Cohen and F. Reif, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 5, p. 531; and T. J. Rowland, *Progr. Mater. Sci.* **9**, 1 (1961). See also, I. Solomon, *Phys. Rev.* **110**, 61 (1958).

<sup>2</sup> T. J. Rowland, *Phys. Rev.* **119**, 900 (1960).

<sup>3</sup> J. Friedel, *Phil. Mag.* **43**, 153 (1952); *Suppl. Nuovo Cimento* **2**, 287 (1958).

<sup>4</sup> W. Kohn and S. H. Vosko, *Phys. Rev.* **119**, 912 (1960).

<sup>5</sup> A. Blandin and J. Friedel, *J. Phys. Chem. Solids* **17**, 170 (1960); *J. Phys. Radium* **21**, 689 (1960).

<sup>6</sup> See, however, P. L. Sagalyn and J. A. Hofmann, *Phys. Rev.* **127**, 68 (1962).

<sup>7</sup> N. F. Ramsey and R. V. Pound, *Phys. Rev.* **81**, 278 (1950).

<sup>8</sup> A. G. Anderson, *Phys. Rev.* **115**, 863 (1959).

<sup>9</sup> L. C. Hebel, *Phys. Rev.* **128**, 21 (1962).

linewidth (10 kc/sec). The failure of the single-frequency technique can be understood from some recent work by Landesman and Goldman on a similar system and by Hartmann and Hahn on a related system. The use of two frequencies is related to and suggested by the technique of 180° phase reversal used by Hartmann and Hahn<sup>10</sup> in their method of double resonance spectroscopy. The detailed theory of the experiment is discussed qualitatively in Sec. III, but a busy reader can omit reading about these details and still understand the results of this research.

Pure quadrupole resonance of Al<sup>27</sup> in aluminum containing zinc impurity has recently been observed independently by N. Fernelius and C. P. Slichter (private communication) using the single frequency<sup>7,8</sup> technique.

## II. EXPERIMENTAL METHODS AND RESULTS

Most of the apparatus used is described in previous publications.<sup>8,11,12</sup> The rf head was the same one described in reference 12 except that the entire He<sup>3</sup> and receiver coil system in that reference was replaced by a simple receiver coil supported and rotatable from above by a metal tube. The 5000 G polarizing field was turned on for 3 sec; the field was off for 0.65 sec and the sf applied for 0.5 sec of this time. Magnetic resonance at 1000 G was swept through about 0.5 sec after cutting off the sf. The sf was supplied to the receiver coil which was switched to this function by a shielded relay. The whole cycle was repeated every 6 sec, as controlled automatically by a complex collection of cam timers, electronic interval timers, delays, and semifunctioning relays.

The sf was generated by two identical independent oscillators whose tuning condensers were motor driven from the same shaft and offset to produce a roughly constant frequency difference  $2\Delta$ . The outputs of these two oscillators were connected to two pentode-connected 807's having separate unbypassed cathode resistors for degeneration, and a common plate load consisting of the untuned receiver coil connected through a suitable coupling circuit. The coupling circuit contained a high-pass filter designed to remove components at the difference frequency  $2\Delta$  which were generated at high power levels in spite of the degeneration in the 807 cathodes. It is important to eliminate such low-frequency components as nearly as possible since the spin system is much more sensitive to them (as is seen below and in reference 8) than to high frequencies.

For low-frequency runs the motor driven oscillators were replaced by either one or two commercial oscillators adjusted by hand. The high-pass filter in the coupling circuit was also removed.

The sf field intensity  $H_s$  was estimated from a meas-

urement of the current sent through the receiver coil and from the receiver coil geometry. It is probably correct to within 30%.

Samples of copper containing Ag, Zn, Al, and Sn were prepared from master alloys containing about 3% of these elements. Samples and master alloys were made by melting in quartz tubes with a torch; the tube was pumped by a mechanical vacuum pump except for the zinc alloys which were melted under argon. Filings were made with a fine hand file; their size is estimated to be about 150 mesh. The filings were cleaned in HCl, sealed in glass tubes under vacuum or argon, and annealed at about 400°C for several hours. A control sample of pure copper was also prepared under the same conditions of purity; no quadrupole resonances were found in it, and we believe that unknown impurities are not a problem considering the low sensitivity of our apparatus. Because of the crudeness of our sample preparation the concentrations of added impurities quoted below are not too reliable, especially in the case of zinc.

Under the conditions of our experiment there are strong competing processes in addition to quadrupole resonance absorption which reduce the magnetic resonance signal after a demagnetization cycle. These are: spin-lattice relaxation at zero field<sup>11</sup>; direct absorption of energy by the spin system from difference frequency ( $2\Delta$ ) component of power generated in the sf circuit<sup>8</sup>; and an important loss of signal which occurred with no sf applied and short magnetic field turn-off time, which we think may be associated with irreversible spin diffusion of the type discussed by Hebel.<sup>9</sup> The signal after a demagnetization cycle was about that corresponding to the signal observed after a 1000-G polarization with no demagnetization, and nearly half of this was due to repolarization of the sample by the 1000-G field before the magnetic resonance signal was measured. The sensitivity was further reduced by instabilities of uncertain origin; the magnetic resonance signal varied randomly by about 3% from cycle to cycle.

Despite the less than optimum sensitivity indicated above it appears that this apparatus could detect the quadrupole resonance of any set of neighbors of impurities not excessively broadened by other imperfections. The optimum value for  $\Delta$  was about 10 kc/sec; at 5- and 15-kc/sec sensitivity was reduced by about 40 and 20%, respectively. Surprisingly, there was little change in linewidth as  $\Delta$  was increased. At high frequencies (>150 kc/sec) the optimum level for the search frequency field is thought to be somewhat greater than was obtainable with our apparatus. Because of the presence of a difference frequency ( $2\Delta$ ) component due to nonlinearities in the sf system at high power, it was difficult to investigate this point quantitatively. At low frequencies the optimum sf level was less than 1 G.

We were surprised to find that the relative intensity and linewidth of our quadrupole resonance at high frequency did not depend strongly on concentration.

<sup>10</sup> S. Hartmann and E. L. Hahn, *Phys. Rev.* **128**, 2042 (1962).

<sup>11</sup> A. G. Anderson and A. G. Redfield, *Phys. Rev.* **115**, 583 (1959).

<sup>12</sup> Y. Masuda and A. G. Redfield, *Phys. Rev.* **125**, 159 (1962).

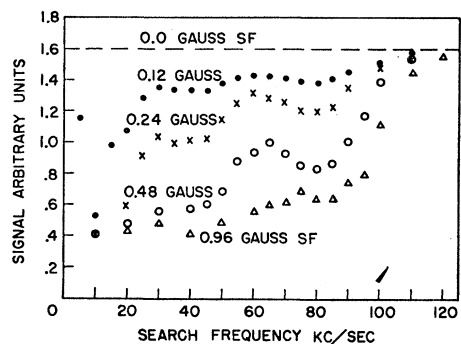


FIG. 1. Single-frequency runs in copper containing 0.05 at. % silver impurity. The ordinate is the high-field magnetic resonance signal observed after the field had been turned off adiabatically, the spins irradiated in zero field at the search frequency, and the field reapplied adiabatically. In this and all other figures the stated sf gauss is the absolute peak value of the search field.

Resonances were easily observed in samples containing 0.25 and 0.05% Ag and 1.0 and 0.2% Zn. The low-frequency single-frequency absorption was more intense, and the low-frequency structure less pronounced, in the more concentrated samples.

A series of low-frequency single-frequency runs on Cu-0.05 at. % Ag is shown in Fig. 1. At higher power levels there is saturation. The best idea of the absorption spectrum is obtained from the difference between the curves in Fig. 1 for low power and the "baseline" for zero power. The detailed interpretation of Fig. 1 will be left until the last section but it can be seen that there is apparently an absorption peak at about 75 kc/sec.

There is a weak residual absorption for a single frequency to greater than 200 kc/sec, but when two frequencies are applied a distinct peak appears at about 200 kc/sec, presumably due to quadrupole resonance of a set of Cu nuclei (Fig. 2).

A search for resonances was carried out up to 2 Mc/sec in this alloy using the two-frequency technique. At 620 and 570 kc/sec there was a pair of resonances having intensity ratios of 2:1 at low power levels, below saturation, and less intense at the same level than the 200-kc/sec resonance. These two resonances are presumably to be identified with  $\text{Cu}^{65}$  and  $\text{Cu}^{63}$ , respectively; these two isotopes have an abundance

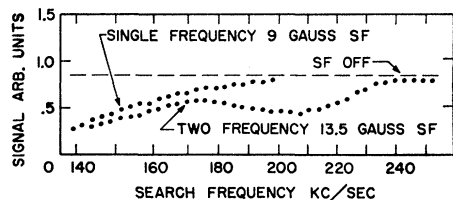


FIG. 2. 200-kc/sec quadrupole resonance in Cu containing 0.05% Ag impurity, as observed by applying two frequencies separated by  $2\Delta = 10$  kc/sec. For comparison a single-frequency run is also shown. The time average of applied search frequency field squared is nearly the same for both runs. The ordinate is the average frequency for the two-frequency run.

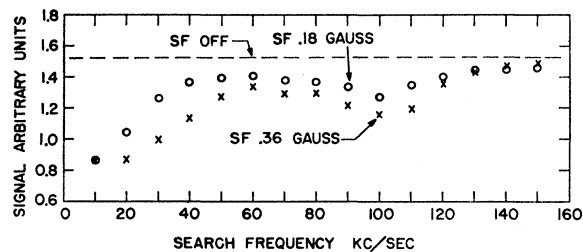


FIG. 3. Single-frequency runs in Cu-0.2% (at.) Zn.

ratio of 2:1, spin  $\frac{3}{2}$ , and quadrupole moment ratio<sup>18</sup> of 1.08:1.0. At 475 and 440 kc/sec there was a similar pair of resonances whose intensity was about half that of the 620/570 kc/sec pair. When these resonances were swept with a single frequency, no absorption was observed.

A set of low-frequency runs on Cu-0.2 at. % Zn is shown in Fig. 3, suggesting a strong resonance at 100 kc/sec. A two-frequency search for resonances was diligently carried out from 140 kc/sec to 5 Mc/sec, and with reduced sensitivity to 6.3 Mc/sec. Surprisingly, only one intense set of resonances was observed at 1980/1810 kc/sec, as shown in Fig. 4.

No resonances or low-frequency structure were observed in Cu-Sn or Cu-Al. In both cases there was broad low-frequency absorption decreasing monotonically with increasing frequency observable up to 200 kc/sec and, in Cu-Sn, increasing in intensity with increasing concentration. We did not try very diligently to find resonances in these alloys by changing our methods of sample preparation. Possibly the impurities added to these samples did not go into solution, or else there was sufficient residual strain to broaden every quadrupole resonance excessively.

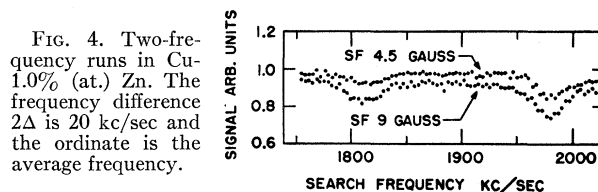


FIG. 4. Two-frequency runs in Cu-1.0% (at.) Zn. The frequency difference  $2\Delta$  is 20 kc/sec and the ordinate is the average frequency.

This latter possibility can be checked by means of a method which was unfortunately not known to us at the time we were studying the Sn and Al alloys. We invented this method when an electronic maladjustment led to the inadvertent application of a 30 G dc field to the Cu-Zn sample during the time when the sf field was applied and the dc field was supposed to be zero. A large resonant dip was seen at around 30 kc/sec, as would be expected in a pure strain-free sample. The existence of such a resonance implies that an appreciable fraction of the copper nuclei are at sites for which the quadrupole interaction frequency is smaller than 30 kc/sec; otherwise the Zeeman resonance would be

<sup>18</sup> H. Kruger and U. Meyer-Berkhout, Z. Physik 132, 171 (1952).

smearred appreciably. This in turn implies that, barring segregation, a large fraction of spins which are near neighbors to impurities feel negligible quadrupole interaction (other than that due to their nearby impurity atom) due to residual strain of other impurity atoms. Note that study of the zero-frequency zero-field resonance,<sup>8</sup> or of the high-field Zeeman resonance, does not give this information.

Preliminary observation of the high-frequency resonances in Cu-Ag was also made using a single oscillator which was square-wave frequency modulated at 5 to 20 kc/sec by an interval of from 20 to more than 200 kc/sec. This system is closer to the phase-modulation system of Hartmann and Hahn than is our two-frequency method. This method was satisfactorily sensitive but the observed widths of the quadrupole resonances were greater, probably due to the rich side bands produced by the modulation.

### III. THEORY OF THE EXPERIMENT

The naive expectation that sf energy absorbed by spins near impurities will be transmitted to the rest of the spin system is based on the idea that the entire spin system is coupled strongly via spin-spin interaction. The total absorption of energy in the absence of saturation effects can be written  $\omega_s^2 f(\omega_s)$ . The function  $f(\omega_s)$  is smeared by dipole-dipole interaction but it is roughly proportional to the number of spins having quadrupole resonance frequencies within a range  $d\omega$  near  $\omega_s$ . The factor  $\omega_s^2$  comes from the fact that the average thermal energy of a spin resonant with the sf is proportional to  $\omega_s^2$ , and this energy is absorbed on the average when the sf field flips a spin.

However, for spins close to impurities there is a bottleneck to such transfer of energy which arises because these spins have no neighbors (other than equivalent neighbors equally saturated by the sf power) which have quadrupole interactions close enough to their own to permit transfer of energy via mutual spin flip transitions. It has been shown experimentally<sup>14,15</sup> in similar systems that mutual flips between two spin systems are strongly inhibited when the difference in resonance frequency between the two species is more than a few times the spin-spin interaction frequency. Thus, the neighbors of Ag which have a 200-kc/sec resonance frequency have no near neighbors whose resonant frequency is closer than 100 kc/sec, and no obvious efficient way to get rid of their absorbed energy. The spins which resonate at 100 kc/sec probably have less populous sets of neighbors within 30 kc/sec which help couple them to the rest of spin system. Probably above about 50 kc/sec there is a partial bottleneck in the transfer of energy, however.

To carry this analysis further we introduce a simplified model and some notation. First, let us suppose that

we have only two types of spins interspersed in our lattice: those in zero magnetic and electric field (the  $A$  system) and those having an electric quadrupole interaction large compared to the spin-spin interaction (the  $Q$  system). It can be argued that this model is unrealistic because in reality the spins of interest near impurities are rather far from those having negligible quadrupole interaction. It should be realized, however, that in zero magnetic field, energy can *spatially* diffuse from far away to the vicinity of impurities via flips involving the  $m = \pm \frac{1}{2}$  levels, of spins having large quadrupole interaction; the problem is the transfer of energy in the  $\pm \frac{1}{2}$  levels to the quadrupole system.

Landesman and Goldman<sup>16</sup> have studied paradichlorobenzene, which resembles our model system rather closely. Their unpublished theoretical analysis justifies, for qualitative purposes, a further simplification which we also wish to make, namely, we replace the quadrupole interaction of the  $Q$  system with a Zeeman interaction. That is, we suppose we have interspersed two kinds of spin, one in zero applied field and the other in large applied field  $H_Q$ , assuming that this is possible even though it is not. We assert that this system adequately illustrates our ideas, and refer the reader to Landesman and Goldman for a treatment of a more realistic system on similar lines. What follows is based on their work and that of Hartman and Hahn<sup>10</sup> on a two-species spin system under double irradiation.

The Hamiltonian of our model system is

$$\mathcal{H} = \sum (\mu_{iz} H_Q + \mu_{iz} H_s \cos \omega_s t) + \frac{1}{2} \sum \mu_{iz} h_{ijz} + \frac{1}{2} \sum \mathbf{m}_j \cdot \mathbf{h}_{jj}'. \quad (1)$$

Here the  $Q$  spin magnetic moment operators are denoted by  $\mathbf{u}_i$ ;  $A$  spins by  $\mathbf{m}_j$ ;  $H_Q$  is a magnetic field which would produce a Zeeman resonance frequency equal to the pure quadrupole resonance frequency; and  $\mathbf{h}_{ij}$  is the dipolar interaction field acting on spin  $i$  due to spin  $j$ .  $\mathbf{h}_{ij}$  is an operator given by

$$\mathbf{h}_{ij} = r_{ij}^{-3} \mathbf{m}_j - \frac{1}{3} \mathbf{r}_{ij} (\mathbf{r}_{ij} \cdot \mathbf{m}_j) r_{ij}^{-5}. \quad (2)$$

We assume that the resonance frequency is high; i.e.,

$$H_Q^2 \gg \text{Tr} h_{ij}^2 / \text{Tr} \mathbf{1}, \quad (3)$$

for all pairs  $i, j$  or  $j, j$  of spins. Generally the sf field will be low:

$$H_s^2 \text{Tr} \mathbf{1} \cong \text{Tr} h_{ij}^2, \quad \text{Tr} h_{jj}^2. \quad (4)$$

In writing (1) we have ignored as unimportant the interaction of  $H_s$  with the  $A$  spins, and the interaction between  $Q$  spins; we have also truncated the second term, the  $A$ - $Q$  spin-spin interaction, in the usual way to eliminate terms which produce non-energy-conserving mutual flips.

It is clear that the arguments of the second paragraph of this section apply to this system, and that the second

<sup>14</sup> A. Abragam and W. G. Proctor, Phys. Rev. **109**, 1441 (1958).

<sup>15</sup> P. Pershan, Phys. Rev. **117**, 109 (1960).

<sup>16</sup> A. Landesman and M. Goldman (to be published); see also Compt. Rend. **252**, 263 (1961).

term will not readily couple the  $A$  and  $Q$  systems. However, the  $Q$  spins will nutate at a rate  $\gamma H_s$  and as a result their neighboring  $A$  spins will feel a spin-spin interaction field varying at this frequency. It might be thought, then, that their reaction to this spin-spin field is like their reaction to an externally applied field of frequency  $\gamma H_s$ , and that the  $A$  spins will heat up.

There is only a germ of truth in this conjecture. To see the whole truth it is necessary to transform to a semirotating coordinate system, that is one rotating with respect to the  $Q$  system at the rf frequency  $\omega_s$  but fixed with respect to the  $A$  system. Such a rotation is generated by the unitary operator

$$S = \exp(i\omega_s t \sum \mu_{iz} / \hbar \gamma). \quad (5)$$

The resulting Hamiltonian (neglecting the counter-rotating sf field) is

$$\mathcal{H}_r = \frac{1}{2} \sum \mu_{iz} H_s + \frac{1}{2} \sum \mu_{iz} h_{ijz} + \frac{1}{2} \sum \mathbf{m}_j \cdot \mathbf{h}_{ij}. \quad (6)$$

Here we assume that we are at resonance ( $\omega_s = \gamma H_Q$ ).

The second term in (6) commutes with neither the first or the last term and thus in this frame of reference we have two coupled systems with a *time-independent* Hamiltonian. Under these conditions our previous arguments<sup>17,18</sup> about thermal equilibrium in the rotating frame are applicable. If the  $A$  system is initially cooled by demagnetization while the  $Q$  system is hot, energy will flow from the  $A$  to the  $Q$  system. But this is what happens only when viewed from the semirotating frame of reference, in which the  $Q$  system experiences only the small field  $\frac{1}{2} H_s$ .  $H_s$  must be less than a few times the spin-spin interaction field if thermal contact is to be maintained between the  $A$  and  $Q$  systems.<sup>14</sup> Since there are not many  $Q$  spins, the energy necessary to cool them to the same temperature as the  $A$  system is small and so the  $A$  system is negligibly heated. After this initial small heating, nothing further will happen to the system.

Hartmann and Hahn used an interesting stratagem to avoid this impasse. They reasoned that the flow of heat from the  $Q$  to the  $A$  system should be finished in a spin-spin relaxation time (several tens of  $\mu\text{sec}$ ). After this time they reversed the phase of the sf power instantly. Before this reversal the  $Q$  spins are slightly polarized along  $\mathbf{H}_s$  as a result of being cooled by the  $A$  spins; afterward they are antipolarized and can be described as having a negative temperature, or as being hotter than infinitely hot. Subsequently heat flows from the hot  $Q$  system to warm up the  $A$  system slightly more. Hartmann and Hahn repeat this phase reversal every  $T_2$  for as long as experimentally possible, heating up the  $A$  system in the course of time at resonance and doing nothing to the  $A$  system if  $\omega_s$  is off resonance.

Any nonadiabatic variation of  $H_s$  with time will

produce such an effect and that of Hartmann and Hahn is probably the most effective type of variation and is essentially a square wave variation of  $H_s$ . Our method differs only in that we use a sinusoidal  $H_s$ : It is easily seen that two fields of frequency  $\omega_s \pm \Delta$  appear, in a reference frame rotating at  $\omega_s$ , to be a field varying sinusoidally at the frequency  $\Delta$ . We tried this method because it was experimentally easy and we thought it would give better resolution owing to the lack of far-out sidebands. The latter conjecture is reasonable theoretically but we have not proven it experimentally. Our method is reminiscent of rotary saturation.<sup>17</sup>

The optimum value of search frequency field is presumably of the order of 15-G peak. Since it is the rms value of rf field component perpendicular to the major axis of the electric field gradient tensor which is effective here, and since one loses a factor of 2 in going into the rotating frame, this gives an rms effective field of about 5 G which is roughly equal to the rms dipolar field. At higher sf levels energy exchange between  $A$  and  $Q$  systems is inhibited because the simultaneous flip-flop of an  $A$  spin against its local field and a  $Q$  spin against its effective field becomes energetically forbidden. At lower sf fields the specific heat of the  $Q$  system decreases, decreasing its effect on the  $A$  system.

The optimum period of sf reversal  $\Delta^{-1}$  is expected to be of the order of  $T_2$ , the spin-spin relaxation time. This conjecture was crudely confirmed experimentally. From what has been said above it might be thought that energy flow between the  $A$  and  $Q$  systems was proportional to the temperature difference between them, and this would lead to an optimum  $\Delta$  equal to infinity (or at least much larger than  $T_2^{-1}$ ), so that the  $Q$  system temperature was infinite. That this is wrong can be seen if our method is viewed as rotary saturation,<sup>17</sup> or by going back to the method of Hartmann and Hahn. In that case, exchange of energy between the  $A$  and  $Q$  systems is expected to be Gaussian in its temporal character, like any spin-spin relaxation process, rather than exponential. Thus, in the limit of short phase reversal time the flow of energy will approach zero, since after each reversal the system is nearly at zero temperature and the energy which has been exchanged is proportional to the square of the pulse length.

#### IV. DISCUSSION

We first treat the identification of the various resonances with different sets of neighbors of the added impurities. In what follows we will always refer to the  $\text{Cu}^{68}$  resonance frequencies.

The fact that the relative intensities of  $\text{Cu}^{68}$  and  $\text{Cu}^{65}$  resonances are roughly as expected from the abundance ratio of these two isotopes indicates that intensities can be used to help identify resonances. Thus in Cu-Ag, the 620-kc/sec resonance is probably due to the 12 nearest neighbors and the weaker 475-kc/sec resonance is due to the 6 next-nearest neighbors. The intense

<sup>17</sup> A. Redfield, Phys. Rev. **98**, 1787 (1955).

<sup>18</sup> See also, C. P. Slichter and W. P. Holton, Phys. Rev. **122**, 1701 (1961); and A. Abragam, *Nuclear Magnetism* (Clarendon Press, Oxford, 1961), Chap. XII.

200-kc/sec resonance is very likely due to the 24 third neighbors. This assignment appears consistent with Rowland's measurements;<sup>2</sup> he found that at 4 Mc/sec each Ag impurity wipes out (in second order) the magnetic resonance of 25 copper spins. This is the number of copper spins having quadrupole interaction greater than 200 to 300 kc/sec. Using the procedure of Sagalyn *et al.*<sup>19</sup> and our measured quadrupole interaction with the assignment above, we estimate a wipeout number of 29 at 4 Mc/sec, which compares favorably with Rowland's experimental value of 25.

The low-frequency data in Cu-Ag (Fig. 1) indicates resonances at 75 kc/sec and perhaps 40 kc/sec. These "resonances" should be taken cautiously because as mentioned in the previous section the absorption in this domain is theoretically proportional to  $\omega_s^2 g(\omega_s)$ , where  $g(\omega_s)$  is the spin spectral density. The factor  $\omega_s^2$  may lead to the appearance of apparent resonant peaks where  $g(\omega)$  drops suddenly, even when  $g(\omega)$  has no resonant peaks. However, such peaks certainly indicate the order of magnitude of resonance frequency of populous sets of neighbors. Thus, the 75-kc/sec peak is probably due to 4th or 5th neighbors while the 40 kc/sec rise may be associated with the populous (48) 7th neighbors. The actual quadrupole resonance frequencies of these neighbors may be somewhat smaller than indicated by these peaks.

In Cu-Zn, Rowland found a wipeout number of 18, strongly suggesting that nearest and next-nearest neighbors have quadrupole interactions which are greater than 300 kc/sec. We find only one resonance above 300 kc/sec, at 1980 kc/sec, so we assume that this is the second neighbor to zinc and that the nearest neighbor has a resonance frequency greater than 5 Mc/sec. It is remotely possible, of course, that the 1980-kc/sec resonance is the nearest neighbor and that the second neighbor has a resonance frequency greater than 5 Mc/sec, or that the second neighbor resonance is broadened anomalously for some reason and is thus unobservable. Rowland's data almost certainly preclude the possibility that the second neighbor has zero field gradient.

There is a very definite peak at 90 kc/sec in Cu-Zn, and a rise around 30 kc/sec. We guess that these are due to third neighbors and fifth or seventh neighbors, respectively, though these identifications are extremely uncertain.

These results are summarized in Table I and compared with the theoretical estimates of Kohn and Vosko of the field gradients due to conduction electron scattering by the impurity, and semiempirical estimates of Sagalyn *et al.* which include the effect of strain near the impurity. These theoretical estimates are not expected to be quantitatively reliable, especially for nearest and next-nearest neighbors.

The observed Cu-Ag resonances confirm estimates of

<sup>19</sup> P. Sagalyn, A. Paskin, and R. Harrison, *Phys. Rev.* **124**, 428 (1961).

TABLE I. Experimental and theoretical values of the electric field gradient (in units of  $10^{23} e \text{ esu/cm}^3$ ) at different neighbor shells relative to the solute atom. The experimental values are calculated assuming that the quadrupole moment of  $\text{Cu}^{63}$  is  $0.157 \times 10^{-24} \text{ cm}^2$ . The sign of the field gradient is not determined in this experiment.

Shell	1	2	3	4	5	6	7
No. of atoms in shell	12	6	24	12	24	8	48
Ag exper.	2.27	1.74	0.73	0.28 <sup>c</sup>	0.28 <sup>c</sup>		0.15 <sup>c,d</sup>
Theor. KV <sup>a</sup>	1.36	0.57	0.30	0.05	-0.16	-0.03	0.09
Theor. SPH <sup>b</sup>	4.56	0.65	0.92	0.45	0.15	0.19	0.26
Zn exper.	>18 <sup>c</sup>	7.25 <sup>c</sup>	0.33 <sup>c</sup>		0.11 <sup>c,d</sup>		0.11 <sup>c,d</sup>
Theor. KV <sup>a</sup>	2.36	-1.06	0.65	0.03	-0.32	-0.02	0.18
Theor. SPH <sup>b</sup>	3.30	-0.57	0.82	0.16	-0.19	0.06	0.22

<sup>a</sup> Charge or conduction electron contribution estimated by Kohn and Vosko, reference 4.

<sup>b</sup> Semiempirical estimate by Sagalyn, Paskin, and Harrison, reference 10.

<sup>c</sup> Assignment uncertain.

<sup>d</sup> Observation of a resonance corresponding to this interaction is uncertain.

strain-induced interaction from Rowland's data. There is as yet no theoretical estimate of the quadrupole interaction due to strain-induced deformation, nor is much known about the details of the atomic displacement near an impurity. It is rather surprising that nearest and next-nearest neighbors have nearly the same interaction; possibly this is a result of interference between strain effects and conduction electron effects, although it is not entirely clear that these two contributions can be separated close to the impurity.

The Cu-Zn interactions must be almost entirely due to conduction electron effects since Zn strains the lattice much less than does Ag. The interaction observed for third and more distant neighbors is in reasonable agreement with theory. The interaction for nearest and next-nearest neighbors appears to be much larger than expected theoretically. However, existing theories<sup>3-5</sup> are expected to be invalid close to the impurity where the conduction electron is highly perturbed, or apply only to free electrons screening a point charge.<sup>20</sup>

It is probable that these near-neighbor interactions involve the virtual excitation of electrons from the  $3d$  bands of copper to unoccupied states in the conduction band. There are several reasons for suspecting this. The quadrupole interaction in the atomic  $3d^{10}4s4p$  state is estimated to be only 10 Mc/sec or less, so that it is difficult to explain an interaction of 2 Mc/sec, particularly for a second neighbor, from conduction band perturbation alone. Relatively little energy is needed to excite a  $d$ -electron to the conduction band (about 2 eV).<sup>21</sup> The  $3d$  electrons produce a large quadrupole interaction; for the atomic  $3d^94s^2$  state the interaction frequency is about 75 Mc/sec.<sup>22</sup>

It should be realized that at short distances virtual excitation to highly excited electronic states must be taken account of, in contrast to large distances for

<sup>20</sup> J. S. Langer and S. H. Vosko, *J. Phys. Chem. Solids* **12**, 196 (1959).

<sup>21</sup> B. Segall, *Phys. Rev.* **125**, 109 (1962).

<sup>22</sup> W. Fischer, *Z. Physik* **161**, 89 (1961).

which only energy-conserving scattering need be considered.<sup>3-5</sup> A situation similar to this one has been discussed by Bloembergen and Rowland,<sup>23</sup> who estimated the electron-coupled spin-spin interaction in an insulator. There, the hyperfine interaction of one spin virtually excites electrons from the valence band to the conduction band; these excited electrons produce a hyperfine field at neighboring spins which falls off rapidly with distance because of interference between different excited electronic states. Their perturbation calculation is not valid here because the impurity presumably is a large perturbation, but it illustrates what may happen near the impurity. It is reasonable to expect that the *d*-band quadrupole interaction for a nucleus a distance *r* from the impurity is given roughly by

$$\nu(r) = \nu_a \exp(-kr), \quad (7)$$

where  $\nu_a$  is roughly equal to the atomic *3d* quadrupole interaction of 75 Mc/sec, and *k* is of the order of the Fermi momentum  $k_F$  for a spherical conduction band. Assuming  $\nu_a$  equal to 75 Mc/sec, *k* would have to be about 0.8  $k_F$  to explain our observed 2-Mc/sec second neighbor resonance.

The *d*-band perturbation might be expected to be much larger for zinc than silver. A zinc impurity perturbs the copper *3d* band greatly because there are no *d* atomic levels in zinc close to the *3d* levels in copper. In silver the atomic *4d* levels are relatively close to the copper *3d* band so that silver may present a minor perturbation to the *3d* band of copper. It would seem that other heterovalent impurities would likewise induce extra large near-neighbor quadrupole interactions.

<sup>23</sup> N. Bloembergen and T. J. Rowland, Phys. Rev. **97**, 1679 (1962).

## V. CONCLUSION

It would obviously be interesting to make a comprehensive study of these resonances for every possible added impurity in copper. It would also be desirable to identify more positively the resonances found in this research.

The ultimate sensitivity of this type of spectroscopy is discussed in detail by Hartmann and Hahn.<sup>10</sup> The improvement in sensitivity over conventional spectroscopy is of the order of  $T_1/T_2$  but at low concentrations there is a decrease in sensitivity because transmission of energy in the majority spin system is spin-diffusion limited. Our apparatus was too unstable to approach the theoretical sensitivity. We believe that in practice an increase in sensitivity of at least two orders of magnitude is possible with carefully designed apparatus, lower temperatures, and signal integration techniques. At that point, residual impurities and imperfections might become a serious problem.

This technique could presumably be extended to single crystals<sup>6</sup> and the direction of the electric field gradient determined. The sign of the field gradient can also be determined in principle<sup>24</sup> though to do so in practice may be difficult.

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<sup>24</sup> A. H. Silver, T. Kushida, and J. Lambe, Phys. Rev. **125**, 1147 (1962).