

Nuclear Magnetic Resonance in Copper Alloys. Electron Distribution Around Solute Atoms*

T. J. ROWLAND

Union Carbide Metals Company, Niagara Falls, New York

(Received March 18, 1960)

The effects of the addition to copper of a wide variety of B subgroup elements on the nuclear magnetic resonance absorption of copper are described. The resonance amplitude, which undergoes a sharp reduction upon alloying, is of special interest; its dependence upon solute valence and size argues decisively in favor of conduction electron charge redistribution (valence effects) as the dominant source of the electric field gradients surrounding these solutes. Furthermore, these gradients are shown to decrease only about as $1/r^3$ rather than exponentially as had been supposed. Using the proportional change in the lattice parameter of the solid solution as a measure of the local strains surrounding a solute atom, only slight correlations between local strains and resonance amplitude were found. It is concluded that the origin of electric gradients around multivalent solutes in copper is almost purely an effect of conduction electron distribution and that this distribution is not of the exponentially screened Coulomb charge type. The spatially oscillating charge distribution derived and recognized by Friedel and recently elaborated by Kohn and Vosko and Friedel and co-workers satisfactorily explains the observations.

I. INTRODUCTION

THIS paper reports the results of a comprehensive experimental study of the nuclear magnetic resonance of copper in a wide variety of copper-base primary solid solutions containing B subgroup elements as solute. These alloys are all of the substitutional type, and have been the subject of numerous thorough investigations of other kinds, a fact which is of considerable importance in interpreting the resonance data. The work to be described was undertaken in an effort to determine the origin of the electric field gradients which surround solute atoms in solid solution. Previous studies of nuclear electric quadrupole interactions in alloys have been too restricted in scope to furnish broad generalizations about the effects of various solute species. It has consequently not been possible to state whether the observed "quadrupole effects" were the result of lattice strains caused by atomic misfit (size effects) or the result of a redistribution of conduction electrons (valence effects). Of the two, the first alternative seems to have been most often assumed.

The nuclear resonance absorption of copper undergoes a striking reduction in amplitude when the metal is alloyed, i.e., when any foreign element is introduced into the copper lattice. The reduction is accompanied by relatively slight changes in the line shape, width, and position. This behavior has been explained phenomenologically¹ as the effect of electric field gradients generated by the solute atoms. The interaction of these gradients with the nuclear electric quadrupole moments perturbs the energy levels of the nuclear dipoles in a magnetic field and shifts their transition energies appreciably. A quantitative description of this effect will be given in Sec. IV, using electric field gradients derived

by Kohn and Vosko² in an accompanying paper referred to henceforth as KV. The theoretical behavior of the nuclear resonance absorption as a function of alloy composition and resonance frequency will then be compared, in Sec. V, with the experimental results presented in Sec. III. The experimental apparatus and techniques will be the subject of Sec. II.

The good quantitative agreement between experiment and theory strongly supports the electron density distribution computed by Kohn and Vosko. This distribution is the result of a self-consistent treatment of the conduction electron charge around a solute atom and does not consider lattice distortions. This fact, together with the poor correlation of the resonance observations with x-ray measurements of lattice dilation, forces us to conclude that inhomogeneous strains introduced by solutes must have a relatively slight influence on the gradients in most of the alloys investigated. Deviations from the behavior predicted by the charge distributions of KV are in the right direction to be ascribed to lattice strains.

During the initial stages of this work, the pertinent question of the role played by the Knight shift arose, and even the extreme possibility that the observed phenomena could be explained entirely on that basis was suggested. The qualitative effects on the absorption line of variations in solute concentration and external magnetic field strength are sufficient to establish the prime importance of quadrupole interactions in determining the resonance behavior of these alloys. A study of the resonance of silver in silver-base alloys³ was undertaken with the sole object of becoming well acquainted with the characteristics to be associated with alloys in which the Knight shift alone was present. The fact that in copper alloys the line width varies little with either solute concentration or external field

* A preliminary account was published in Bull. Am. Phys. Soc. **5**, 176 (1960).

¹ N. Bloembergen and T. J. Rowland, Acta Met. **1**, 731 (1953).

² W. Kohn and S. H. Vosko, following paper [Phys. Rev. **119**, 912 (1960)].

³ T. J. Rowland (to be published).

strength is contrary to the behavior expected of the Knight shift. Also, we note that it would be exceedingly unlikely for a change in the Knight shift of more than ten percent to take place even at nearest neighbor sites.⁴ The shift involved in the alloys under discussion would be only about one kilocycle (less than $\frac{1}{3}$ of the line width of copper) at most, and could not possibly be large enough to be interpreted as the intensity changes which are a primary characteristic of the results. In addition, we have the fact that annealing increases the intensity of the resonance in *pure* copper by a factor of 2.5 from its value for heavily cold-worked copper. This must be ascribed to (first order) quadrupole interaction, not the Knight shift.

II. EXPERIMENTAL PROCEDURES

The experimental apparatus used was largely of standard design. Two commonly used detection schemes⁵ were employed, the choice in any particular instance being based on the relative importance of the resonance parameters to be measured. The Bloch nuclear induction method was used for practically all of the amplitude and line width studies. The Pound-Knight-Watkins circuit was often used to check line width determinations and to obtain data for line shape studies. For the latter, a faithful reproduction of the nuclear absorption is especially desired. The rf probe coils were, in every case, wound with pure silver. The output of the rf unit in use went directly into a detector, audio amplifier, narrow band amplifier, phase-sensitive detector, output integrating circuit, and recorder. Audio modulation was applied to the external magnetic field so the above detection circuits produced a dc output closely proportional to the derivative of the resonance curve. Output time constants between 3 and 30 seconds were commonly used, with longer integrating times, and correspondingly lower sweep rates, being required to maintain a good signal-to-noise ratio for the measurements on the more concentrated alloys. A relatively low amplitude of rf field (peak circular $H_1=0.06$ gauss) was used to avoid saturation effects which include aggravating the out-of-phase audio components encountered upon phase-sensitive detection.⁶ The frequency of the audio modulation was restricted to 20 or, at most, 40 cps for the same reason. The audio modulation amplitude generally used was 2.1 gauss peak-to-peak, somewhat less than $\frac{1}{3}$ of the line width for copper and its alloys, and aluminum.

As mentioned above, a marginal oscillator was sometimes used in preference to the nuclear induction apparatus in order to avoid inadvertently obtaining a mixture of the nuclear absorption and dispersion. Fortunately, slight asymmetries in the resonance,

introduced by imperfect adjustment of the leakage voltage which is mixed with the nuclear absorption signal in the crossed-coil method, have almost no effect on the peak-to-peak derivative amplitude,⁷ and their presence usually could not offset the advantages of the induction apparatus, particularly its ready adaptability to routine measurements and somewhat more dependable operation with metal powders. Since a mixture of absorption and dispersion can result from particle size effects also,⁸ the alloys used in this investigation were filed and the filings passed through either a 200- or 325-mesh sieve, depending upon their composition (hence resistivity) and the frequency at which the resonance was to be observed. Most of the 4 Mc/sec data were obtained using 200-mesh particles since microscopic examination showed their smallest dimensions to be less than the skin depth. The resistivities of the various alloys range from about 2μ ohm-cm for 1 atomic percent zinc to 27μ ohm-cm for 4 atomic percent arsenic.

The external magnetic field was supplied by a Varian 12-inch electromagnet and its associated current regulated power supply. The field inhomogeneity over the sample (≈ 0.1 gauss) was negligible compared to the line widths being observed. During most of the work, the external field was swept through the resonance and the frequency held constant; at times, however, when using the Pound oscillator, the frequency was swept instead. In no essential way does this change affect the outcome of the measurements to be discussed.

The alloys were prepared over a considerable period of time from two different batches of copper. Although this was not intentional, it was reassuring to find that the change from OFHC copper⁹ to 99.999 copper during the latter part of this work had no discernible systematic effect on the measurements. This can probably be ascribed to the fact that the total impurity content of the OFHC copper was negligible when compared to the solute concentration in these alloys. The solute metals were all of high purity (Ga, In, Zn > 99.999; Ag, As, Au, Cd, Ge, Ni, P, Sn > 99.99; Al, Mg, Si > 99.9; Sb 99.8), although this was not of major concern because even a 99.5% pure solute would introduce only 0.005*c* of foreign impurity (*c*=solute concentration). With few exceptions (to be discussed below), the alloys were prepared in 40- to 60-gram quantities by melting the weighed constituents under about one atmosphere of argon in sealed quartz capsules. The argon discourages the migration of volatile solutes from the surface of the ingot during subsequent heat treatment. The molten

⁷ This is an experimental observation which has been verified by an analysis similar to that of Seymour et al. (reference 8).

⁸ N. Bloembergen, J. Appl. Phys. **23**, 1383 (1952); A. C. Chapman, P. Rhodes, and E. F. W. Seymour, Proc. Phys. Soc. (London) **B70**, 345 (1957).

⁹ Spectrographic analysis of this copper showed parts per million of iron, tin, lead, and silver, and less than 0.01% nickel; no other metallic impurities were present in detectable quantity. It is a pleasure to acknowledge this generous (20 pound) gift from The American Brass Company, Buffalo, New York.

⁴ A. Blandin and E. Daniel, J. Phys. Chem. Solids **10**, 126 (1959).

⁵ E. R. Andrew, *Nuclear Magnetic Resonance* (Cambridge University Press, New York, 1955).

⁶ A. G. Redfield, Phys. Rev. **98**, 1787 (1955).

alloys were agitated periodically for about two hours before being cooled in an air blast, then, without breaking the capsule, they were immediately placed in an annealing furnace, the temperature of which was chosen so as to be just safely below the solidus of that particular alloy. The phase diagrams in Hansen¹⁰ were used to determine the appropriate temperature. This anneal was meant to smooth out composition inhomogeneities which occur on solidification and the annealing times were generally days or weeks, depending largely upon the temperature used. In many cases the heat treatments used by the investigators who determined the lattice parameters of copper-base solid solutions were available in the literature and were consulted as a guide to the establishment of equilibrium. After this high-temperature anneal, the ingots were usually quenched by breaking the quartz under oil. One or two small pieces were then cut from the ingot, polished metallographically, and inspected for any signs of a second phase or of coring. None of the alloys for which data are reported showed either of these large scale inhomogeneities. The analysis of the results in a subsequent section applies to random solid solutions; hence, every attempt was made to achieve the high-temperature equilibrium state of these solutions. The presence of macroscopic segregation would always cause the measured intensity to be greater than it would be for a homogeneous solution. Calculations based on various assumed solute distributions have shown that macroscopic concentration fluctuations of ± 0.3 atomic percent would cause increases of approximately 1% in the measured intensity. The change is zero to first order because any solute distribution must have the bulk concentration c as its mean.

After microscopic examination, the alloys were filed and the filings repeatedly passed through a strong inhomogeneous magnetic field to remove stray ferromagnetic particles. The filings were then passed through a sieve, as mentioned previously; they were usually not annealed. In a few instances when filings were annealed, it was found that the intensities before and after annealing were the same, within experimental error. This observation agrees with the accepted notion that dislocations alone are not capable of producing large enough field gradients at enough sites to have a significant effect on the intensity of the central component, although they can drastically decrease the satellite contribution. Since the satellites are already completely obliterated in the alloys under consideration, the dislocations have no effect.

The alloys of Cu with P, Si, and Mg were prepared by other methods. For phosphorus, a master alloy of 8.3 weight % P (eutectic composition) was first made, by reacting red phosphorus vapor with copper chips. This was diluted to form the desired solid solutions. A Cu-4.68 weight % (≈ 10 at. %) silicon master alloy

was made in quartz in an induction heating unit and used to form the more dilute Cu-Si alloys. The Cu-Mg alloys were the only ones which were not made in quartz capsules. These were produced under one atmosphere of argon in graphite crucibles by plunging the magnesium beneath the surface of molten copper with a graphite rod. The melts were then stirred and cooled as soon as possible; the ingot was sealed into quartz and annealed in the usual fashion. The finished alloys were chemically analyzed for magnesium.

In order to derive the desired amplitude data from the derivatives of the absorption curves of the Cu⁶³ in these solid solutions, a reference standard was included with each one during the measurement. The reference consisted of a small (4 mm i.d.) sealed glass sphere containing filings of pure aluminum. The latter provided a reproducible absorption with which to calibrate the apparatus. Copper resonance derivative amplitudes were always compared directly with this reference and measured as a multiple of it. This arrangement satisfactorily compensates for unintentional variations in over-all receiver and lock-in gain as well as audio modulation and rf field amplitudes. It also corrects for changes in the Q of the receiver input circuit which accompany the insertion of the various metallic powders. Extensive subsidiary experiments were conducted to determine the extent to which the standard (and, equally important, the portion of the alloy powder at the center of the sample) was shielded by the surrounding filings. Since the sample geometry chosen was that of a right circular cylinder, it was necessary also to determine the effect of the length of the column of sample and of small deviations in the placement of the sample relative to the rf coils. A depth of sample was used which struck the best compromise of linear output signal with depth, insensitivity to small changes in sample placement, and reasonable requirements on the quantity of powdered alloy to be prepared. The latter stipulation may appear somewhat unscientific, but in view of the number of alloys investigated and the objectives of the investigation, it was an important consideration. Since the rf field geometry in the vicinity of the sample must be unchanged from measurement to measurement, the *volumes* of the samples were made equal. Each sample then consisted of a right circular cylinder 1.4 cm in diameter and 0.7 cm high which could be placed so that its center coincided with the center of the receiver coil. A jig was used to assure reproducibility of placement. The weight of each sample was determined and used to correct the measured amplitude for differences in the amount of contained copper. The symbol J will be used to denote the relative amplitude corrected to equal numbers of copper nuclei; accordingly, $J_{\text{Cu}} = J_{\text{Cu}}' / (J_{\text{Al}}' \times \text{weight of copper in sample})$. Here J_{Cu}' is the directly measured peak-to-peak amplitude of the *derivative* of the absorption curve of copper in the alloy and J_{Al}' is the similarly defined amplitude from the reference. As will be shown in more

¹⁰ M. Hansen, *Constitution of Binary Alloys* (McGraw-Hill Book Company, Inc., New York, 1958).

detail later, in the present context J' is *not* interchangeable with the peak height of the absorption curve itself. In fact, J' is essentially a measure only of that portion of the nuclear absorption which peaks in the vicinity of the resonance frequency ν_0 , characteristic of the pure metal. The majority of the data was obtained at a single frequency (4 Mc/sec); however, in specific cases the frequency dependence of the resonance amplitude was investigated by one of two methods. For the most critical work 325 mesh aluminum filings were thoroughly mixed with the copper alloy powder since it was necessary to change the rf probes, and thus the coil-specimen configuration, in covering the frequency range 2-12 Mc/sec. At other times the reference resonance was obtained from a separate quantity of aluminum powder as described above.

Intensity measurements made with the marginal oscillator used the calibrator circuit of Watkins¹¹ to introduce a dummy absorption as a comparison standard. This technique has been widely used and can be equivalent to the method outlined above, but is probably less reliable over long periods of time unless close attention is paid the components of the calibrator. This method, as the previous, requires careful control of geometry and sample volume, with a correction being applied to make up for variations in the number of copper nuclei in the samples.

III. EXPERIMENTAL RESULTS

From three to nine different compositions of each binary solid solution were made and no less than four

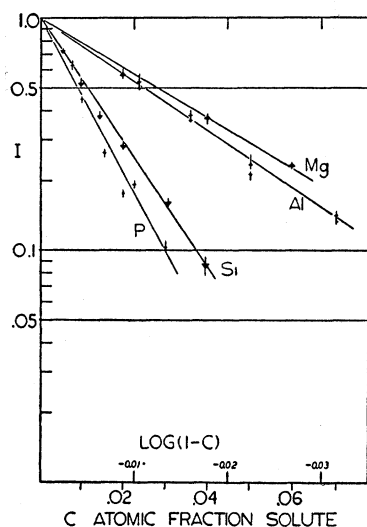


FIG. 1. The effect of third period solutes on the intensity of Cu^{63} at $\nu_0 = 4$ Mc/sec. The length of the vertical lines indicates the actual spread in the observations; the crossbars indicate the average of all observations. The data for Al were obtained using both the Bloch and Pound techniques.

¹¹ A version of this circuit can be found in Fig. 3 of R. V. Pound's article in *Progress in Nuclear Physics* (Pergamon Press, London, 1952), Vol. 2.

independent relative amplitude determinations made on each composition. By "independent determination" is meant a complete recording of the copper and aluminum resonances starting with the reference and alloy separated and out of the field. Scatter of the measurements for any one alloy never exceeded $\pm 10\%$ of the corresponding intensity and was usually within $\pm 5\%$. If the whole sample-standard configuration was left undisturbed in the magnet between field passages, the amplitudes could be reproduced within about 2%. Data were obtained for pure annealed and unannealed copper as well as for the alloys, and all of the amplitudes J divided by the corresponding figure for heavily cold-worked copper, which is virtually equal to $0.4 J_{\text{ann. Cu}}$. The term intensity, I , will be used to denote the relative amplitudes on this scale. Copper containing no solute but having sufficient internal strain to obliterate all satellites has unit intensity.

Figures 1, 2, and 3 display the Cu^{63} intensity as a function of composition for solute elements of Periods III, IV, and V in the Periodic Table and summarize the major results of this investigation. The measurements for Ag, Au, and Ni as solutes appear in Fig. 4. The straight lines have a clear and useful interpretation.¹ They describe the behavior of the intensity which would follow from the assumption that each solute atom causes gradients large enough to render the Cu^{63} resonance unobservable at just n lattice sites. Their slopes n thus succinctly express the relative effect of a given solute on the resonance intensity of copper. As the analysis to follow will show, the lines may represent only an approximation to the actual

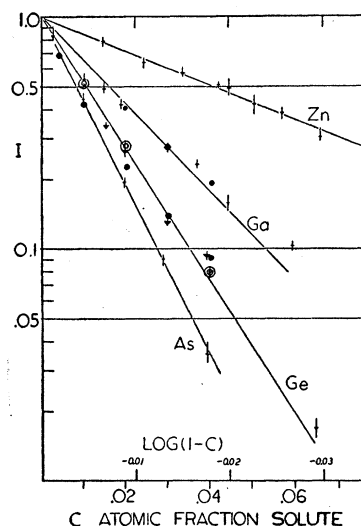


FIG. 2. The effect of fourth period solutes on the Cu^{63} absorption when $\nu_0 = 4$ Mc/sec. The experimental data are given by the vertical lines (see caption, Fig. 1). Three computed intensities for Ga and five for Ge are given (points) using $q_s = 1.5 \times$ (value in Table III of KV). Open circles depict the result of using $q_s = 1.06 \times$ (value of KV) to obtain I vs c , then subtracting $n_s c P_4^*(c)$ from I as discussed in the text. Similar calculated results for As are omitted.

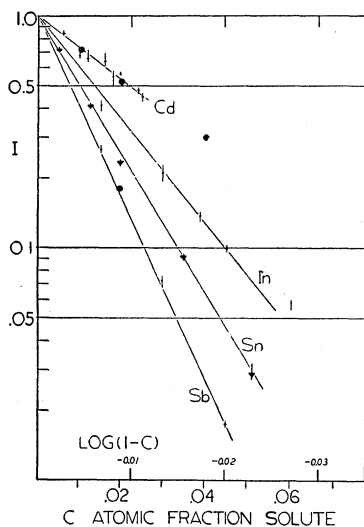


FIG. 3. Experimental and theoretical results for fifth period elements at $\nu_0=4$ Mc/sec. The points represent computed intensities using $q_s=1.5\times$ (value in KV) for Cd and Sb.

dependence in that the intensity as a function of solute concentration c does not necessarily follow the $(1-c)^n$ behavior described by them. In fact, the intensity depends upon the details of the electron distribution, but quite often it can be closely approximated by this simple function which undoubtedly conveys the essence of the situation. For the sake of brevity, we will often speak of the lines as representative of the data.

The most significant characteristic of these results is the marked correlation between the slope n of the I vs c curves and the group to which the solute belongs. This correlation, which is now so evident and so credible that it might easily be passed off as trivial, was unsuspected at the outset of this work. From it we draw two very important conclusions; namely, that the excess charge on a solute atom is most often responsible for the electric gradient which exists in its neighborhood, and that this gradient derives from an electron density distribution of the approximate form Z'/r^3 surrounding the solute rather than the exponential form which is the familiar result of the Fermi-Thomas treatment of this problem.¹² Here Z' is the valence difference between the solute and copper.

The first conclusion results directly from consideration of Table I; we use n as a measure of the electric field gradient generated by each kind of solute. It has often been assumed that local lattice strains, via solvent ion core distortion, caused the electric field gradients around solute atoms.^{13,14} However, using for comparison

¹² N. F. Mott, Proc. Cambridge Phil. Soc. **32**, 281 (1936); L. C. R. Alfred and N. H. March, Phil. Mag. **46**, 759 (1955); H. Fujiwara, J. Phys. Soc. (Japan) **10**, 339 (1955); J. Friedel, *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1954), Vol. 3, p. 446.

¹³ N. Bloembergen, *Report of Conference on Defects in Crystalline Solids, Bristol, 1954* (The Physical Society, London, 1955), p. 1.

¹⁴ M. H. Cohen and F. Reif, *Solid-State Physics*, edited by F.

one of the best measures of atomic displacement, namely, the proportional change in lattice parameter upon alloying, which itself contains an electronic contribution,¹⁵ we find very little correlation with the observed gradients in copper alloys. In treating the displacements around spherical defects by elasticity theory, the proportional change in lattice parameter $(1/a)(da/dc)$ is used¹⁶ to obtain a value for the strength C of the center of dilatation. This constant depends upon the relative atomic sizes of the solute and solvent and is, in the case of an infinite isotropic elastic continuum, given by¹⁶ $C=(3a^2/16\pi\gamma')(da/dc)$, where the constant $\gamma'\approx 1.5$. The resulting radial strain around the defect is simply $\epsilon=C/r^3$ and we would suppose $n\propto C$, and therefore to $(1/a)(da/dc)$. It is apparent from Table I that this is not the case; the correlation between n and $(1/a)(da/dc)$ is poor. Even worse is the correlation between n and the Pauling radii or other commonly used atomic radii.¹⁷

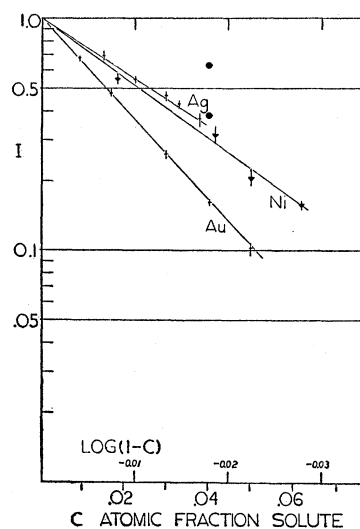


FIG. 4. Measured intensities for elements of $Z'=0$ and Ni at 4 Mc/sec. Computed intensities are given for $c=0.04$ using $q_s=1.5\times$ (value in KV) for Ag (upper point) and Au (lower).

Since the Pauling value refers to a closed core radius, it seemed reasonable to anticipate some correlation with n if core contact or interaction were involved. It is taken for granted that the meaning of atomic size in the present context is obscure; we should like to point out, however, that nuclear resonance does *not* appear to be a promising method by which to investigate this quantity in non-transition metals.

The correlation between n and the group to which

Seitz and D. Turnbull (Academic Press, New York, 1957), Vol. 5, p. 321.

¹⁵ E. A. Owen, J. Inst. Metals **73**, 471 (1947); G. V. Raynor, Trans. Faraday Soc. **45**, 698 (1949); W. B. Pearson, Can. J. Phys. **35**, 358 (1957).

¹⁶ J. D. Eshelby, *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1956), Vol. 3, p. 79.

¹⁷ F. Laves, *Theory of Alloy Phases* (American Society for Metals, Cleveland, Ohio, 1956), p. 124, especially Table III.

the solute belongs is, on the other hand, generally quite good. This is emphasized by the near constancy of n/Z' , taking as Z' the difference between the solute group number and one, and leads directly to our second conclusion; namely, that the electric gradient eq is proportional to eZ'/r^3 . In that case, since the same value of gradient will be found at the same Z'/r^3 for various solutes, the number of spins inside of the sphere of radius r around the solute, namely, $n = 4\pi r^3/3V_0$, will just be proportional to Z' . Here V_0 is the atomic volume and the sphere is a surface of constant gradient. This is equivalent to the statement that the spheres defined by $q = \text{constant}$ have radii proportional to $Z'^{1/3}$ so that their volumes are directly proportional to Z' , in agreement with observation.

TABLE I. Comparison of the effects of various solutes in copper upon its resistivity ρ , lattice constant a , and nuclear resonance intensity. The latter, represented through n , is a measure of the electric gradients surrounding a solute, as discussed in the text. Also included are the Pauling radii.

Solute	Z'	n^a	$\frac{n}{Z'}$	$\left(\frac{\Delta\rho}{c}\right)_{c \rightarrow 0}^b$	$\frac{1}{a} \frac{da}{dc}^c$	Ionic radii ^d (Pauling)
Mg	1	23	23	0.65	0.17	0.65
Zn	1	18	18	0.32	0.056	0.74
Cd	1	32	32	0.30	0.219	0.97
Al	2	27	14	1.25	0.072	0.50
Ga	2	38	19	1.42	0.079	0.62
In	2	48	24	1.06	0.256	0.81
Si	3	61	20	3.95	0.019	0.41
Ge	3	63	21	3.79	0.091	0.53
Sn	3	67	22	2.88	0.271	0.71
P	4	75	19	6.7	0.029	0.34
As	4	80	20	6.8	0.129	0.47
Sb	4	87	22	5.4	0.305	0.62
Ag	0	25	...	0.14	0.12	1.26
Au	0	44	...	0.55	0.15	1.37

^a All values pertain to 4 Mc/sec intensity measurements made at room temperature.

^b In $\mu\text{ohm-cm/atomic percent impurity}$, taken from A. N. Gerritsen, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 19, p. 137.

^c In $(\text{atomic fraction})^{-1}$, from data collected in W. B. Pearson, *A Handbook of Lattice Spacings and Structures of Metals and Alloys* (Pergamon Press, New York, 1958).

^d In angstrom units; N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Clarendon Press, Oxford, 1953), p. 269. The corresponding value for Cu is 0.96A.

Having established the dependence of q upon Z' , the inverse cube dependence of q on r was surprising and puzzling. The redistribution of conduction electron charge which takes place around a positive point charge in the free electron gas will surely screen the positive charge. In fact, the Fermi-Thomas solution of the problem predicts exponential shielding and a gradient which falls below the value required to explain the present results within the first 2 or 3 shells. It rapidly becomes at least two orders of magnitude too small to explain the data. A second consequence of this model is a marked insensitivity of n to Z' . Because of the slight increase in r necessary to compensate [so that $Z'f(r) = \text{constant}$] for an increased Z' , the volume within our sphere of constant q increases very slowly with Z' . The predictions

of the Fermi-Thomas model are thus in almost complete disagreement with experiment.

A satisfactory solution which provides both the necessary charge dependence and $1/r^3$ properties had been noticed by Friedel¹⁸ but was not emphasized because it was thought that these long-range disturbances were of no importance in determining experimentally observable quantities. The effect which Friedel had pointed out was a spatial oscillation of the conduction electron density surrounding a point charge (solute atom). The oscillation has a wavelength of π/k_F ; its amplitude diminishes as $1/r^3$ and is essentially proportional to Z' ; k_F is the Fermi wave number. Both positive and negative deviations from the value of the electron density in the absence of the solute atom are produced but are not differentiated by the present experiments. The oscillations appear as a result of a proper self-consistent treatment of the electron gas surrounding the solute. We shall proceed to examine the balance of the experimental work, assuming that the origin and general behavior of the gradients are in accord with this picture, as developed in KV.

Plots of intensity vs solute concentration at various external field strengths, shown for the alloys Cu-Ge and Cu-Sn (Figs. 5 and 6), exhibit the increasing intensities which always accompany higher external fields. The dependence is qualitatively what one might expect as the second-order-perturbed central transition absorptions collapse toward ν_0 . Careful measurements of line width as a function of external field using a 1 at. %

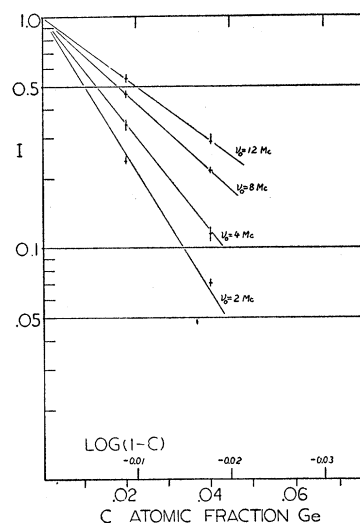


FIG. 5. Experimental data showing the effect of frequency on intensity for two Cu-Ge alloys. The interpretation of this type of study is complicated by the fact that deviations from straight line behavior (if they exist) are obscured by experimental error. It must be remembered that the concept of n vs ν_0 is useful only in the same approximation that the data can be represented by the numbers n .

¹⁸ J. Friedel, *Phil. Mag.* 43, 153 (1952); *Suppl. Nuovo cimento* 2, 287 (1958).

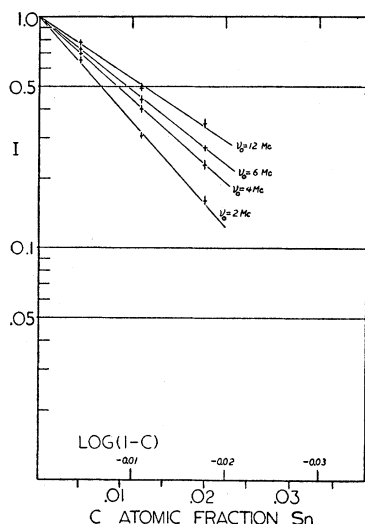


FIG. 6. Measured intensities for alloys of Cu with 0.5, 1.25, and 2.0 atomic % Sn for ν_0 from 2 to 12 Mc/sec. Using the data, a plot of n vs ν_0^{-1} roughly obeys $n = 134 \times 10^3 / \nu_0^{-1}$.

Ge alloy revealed a slight ($< 4\%$) increase in the width in going from 3500 to 12 000 oersted. The small shifts in the line center which were found at 4 Mc/sec are thought to be a consequence entirely of quadrupole interactions, but in any case, considering the uncertainties in the measurements and the line shape calculations, they do not seem worthy of further concern at this time. It is unlikely that the Knight shift plays any part here; in principle, of course, one could, by studying the frequency dependence of the shift with respect to pure copper, discover at least which effect dominates since they give rise to changes of opposite sign, i.e., at higher fields the alloy line should approach pure copper if the quadrupole effects dominate and move away from it, if the Knight shifts dominate. The effect should be most pronounced for the solute elements of highest valence.

The qualitative description of the experimental evidence leads us to conclude that it is necessary to consider the effect of the solute in causing quadrupole interactions only. Changes in the resonance which might be caused by dipolar interactions of one sort or another are inconsiderable.

IV. CALCULATION OF ABSORPTION LINE SHAPE AND INTENSITY

The effect of nuclear quadrupole interactions on the magnetic resonance in alloys is explained by applying perturbation theory to the energy levels of the nuclear magnetic dipole moments in the magnetic field H . The required theory has been given by Pound¹⁹ and has been the subject of an extensive review by Cohen and Reif.¹⁴ Copper has two isotopes, Cu^{63} and Cu^{65} , both of which have a spin of $\frac{3}{2}$. Their magnetic dipole and

electric quadrupole moments differ by less than 10%; however, Cu^{63} is more than twice as abundant as Cu^{65} and so has been used in making the measurements. Where it is necessary in the following to specialize the discussion or quote numerical data, it is Cu^{63} to which reference is made.

In pure, well annealed, metallic copper, most of the nuclei are found at sites of perfect cubic symmetry; at these sites the electrostatic energy of a nucleus is independent of its orientation relative to the crystal axes and the electric field gradient vanishes. Since the quadrupole interaction energy is proportional to the electric gradient at the nucleus, there are no shifts in the energy levels in this case. The absorption line width (between points of maximum slope) is 7.2 kc/sec, contributed almost entirely by direct dipolar interaction. The absorption is perfectly symmetric, with a shape closely resembling a Gaussian curve. Its center lies at the unperturbed resonance frequency ν_0 . Insertion of foreign atoms into the lattice alters this situation by causing deviations from the microscopic cubic symmetry at the lattice points, thus determining a preferred direction for the now inhomogeneous electric field. The resulting gradients cause shifts in the energy levels^{13,14} and consequent changes $\Delta\nu_m$ in the transition frequencies, all of which previously were equal to ν_0 . These changes, in the case of an inhomogeneous electric field of axial symmetry, are given to first order by

$$\begin{aligned} \Delta\nu_m &= \nu_{m \rightarrow m-1} - \nu_0 \\ &= (2m-1)(3 \cos^2\theta - 1)3e^2qQ/8I(2I+1)\hbar. \end{aligned} \quad (1)$$

Here m is the magnetic quantum number describing the orientation of the nuclear spin I , θ is the angle between the axis of symmetry and the direction of the applied magnetic field, Q is the nuclear electric quadrupole moment, which for Cu^{63} is 0.157×10^{-24} cm² (Smith,²⁰ Table I), and e and \hbar have their usual meaning. The scalar quantity

$$q = \frac{1}{e} \left[\frac{\partial^2 V}{\partial Z^2} - \frac{1}{3} \nabla^2 V \right], \quad (2)$$

given in somewhat different form by equation (2.27) of KV, defines the magnitude of the electric field gradient at the nucleus. It is the value of the gradient in the direction of maximum gradient, the axis of cylindrical symmetry.

In the metallic copper lattice, with the concentration of the solutes which we consider, the interactions e^2Qq/\hbar are everywhere so large that the transitions $m = \frac{3}{2} \rightarrow \frac{1}{2}$ and $-\frac{1}{2} \rightarrow -\frac{3}{2}$ never contribute perceptibly to the intensity near ν_0 . The $m = \frac{1}{2} \rightarrow -\frac{1}{2}$ transition is, on the contrary, unaffected according to (1). Its displacement from ν_0 can be calculated using second-order

¹⁹ R. V. Pound, Phys. Rev. **79**, 685 (1950).

²⁰ K. F. Smith, *Progress in Nuclear Physics*, edited by O. R. Frisch (Pergamon Press, New York, 1957), Vol. 6, p. 52.

perturbation theory and is

$$\Delta\nu_{\frac{1}{2}} = \nu - \nu_0 = (A/h)(1 - 9 \cos^2\theta)(1 - \cos^2\theta), \quad (3)$$

in which

$$A = \frac{9}{64} \frac{2I+3}{4I^2(2I-1)} \frac{e^4 q^2 Q^2}{h\nu_0}.$$

In a powdered material, the transition frequency ν described by (3) lies within the region between $\nu_0 - (16A/9h)$ and $\nu_0 + (A/h)$, corresponding to various relative orientations of electric field axis and external magnetic field. The absorption as a function of frequency for a large number of randomly oriented particles has a characteristic shape,^{21,14} depicted by the full line in Fig. 7, which can be expressed analytically by

$$I_s^1(\mu) = \frac{\alpha p}{12(16/9 + \alpha p \mu)^{\frac{1}{2}} [5/9 \pm \frac{1}{3}(16/9 + \alpha p \mu)^{\frac{1}{2}}]^{\frac{1}{2}}}, \quad (4)$$

where $\mu = \nu - \nu_0$, $\alpha = 64h^2/3e^4Q^2 = 7.23 \times 10^{35}$ for Cu⁶³ and $p = \nu_0/q^2$. Note that the useful quantity $A/h = 1/\alpha p$. Clearly the distance between the end points of this curve depends only upon A , and for a specific isotope upon q^2/ν_0 . In a solid solution q will not be the same at each solvent nucleus but will depend upon the location of the surrounding solute atoms. Assuming the gradients eq_1, eq_2, \dots, eq_s , at the first, second, \dots, s consecutive solvent sites in order of distance from a solute atom are known, it is a straightforward matter to compute the resultant absorption curves $I_s^1(\mu)$. The superscript 1 signifies that only one solute is responsible for the gradient eq_s .

The long-range nature of the quadrupole interaction being treated here makes it desirable to consider the effects of all solute atoms out to and including the tenth neighbor shell. In the face-centered cubic lattice, this includes a group of 200 atoms. Beyond this, the interactions are small and have no effect on the resulting computed line shape. In principle, we should consider each configuration of solute atoms which might occur, compute the gradient and line shape resulting from it, then add this contribution (properly weighted for the probability of its occurrence) to all other ones in order to derive the total absorption spectrum. The compositions used for most of this work were in the 0.5 to 5.0 atomic percent solute range, so that the number of reasonably probable configurations is so numerous that the problem as stated is unmanageable. The majority of these configurations would, in addition, introduce field gradients having lower than cylindrical symmetry and thus require the inclusion of a more complex line shape analysis for the individual components. This refinement is hardly justified at present since it would be expected to have an effect comparable in magnitude to that of the other approximations made in the course

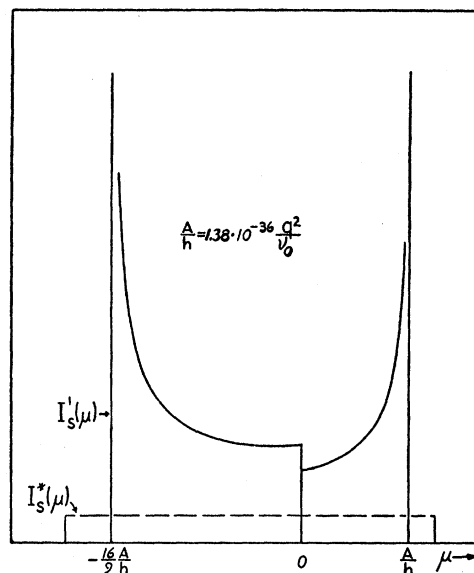


FIG. 7. Theoretical absorption line shape $I_s^1(\mu)$ for a polycrystalline sample with the same axially symmetric electric field gradient at each Cu⁶³ nucleus. The function $I_s^*(\mu)$ is 5/4 wider and approximates the smearing of I_s^1 which takes place in the alloy. The relative amplitudes are distorted here; actually, both are normalized. The ratio of their probabilities of occurrence $P_s^1(c)/P_s^*(c)$ lies between 10 and 0.2 in the composition range we consider (0-6 at. % solute). In the more dilute solutions $P_s^1(c) > P_s^*(c)$.

of calculating the gradients. These more complex line shapes resemble the one described by the full line in Fig. 7 by continuity, since the latter represents the extreme case of an asymmetry constant¹⁹ η equal to zero. The calculations are made in a manner which takes advantage of this similarity by lumping together the effects of configurations which, in most cases, cause gradients differing relatively little from a particular well defined configuration. Since the major effect of the multiplicity of possible atomic arrangements is to smear out the otherwise sharp spectrum, all of these related configurations are supposed to contribute an absorption $I_s^*(\mu)$ described by the dashed line in Fig. 7. All possible configurations are thus separated into two representative types, a well defined, simple configuration, and the totality of all more complex configurations representing variations from it.

The simple configuration (Type I) is defined as one in which a copper atom at the origin is surrounded only by copper atoms out to shell s , which contains one and only one solute atom; also, we require that shell $s+1$ contains only copper atoms. Gradients generated by more distant solute atoms are neglected. The other configuration considered (Type II) is one in which we find either (a) more than one solute in shell s , and none or more in $s+1$, or (b) one in shell s and one or more in $s+1$, i.e., all other configurations giving about the same gradient but having lower symmetry in general. For a random solid solution, the probability of the simple configura-

²¹ T. J. Rowland, Acta Met. 3, 79 (1955).

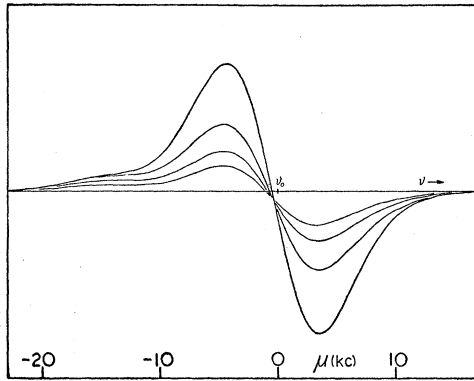


FIG. 8. Calculated Cu^{68} absorption derivative curves for Cu alloys containing (in order of decreasing amplitude) 1.0, 2.0, 3.0, and 4.0 at. % Ge. Here $\nu_0 = 4$ Mc/sec and gradients 1.5 times those found in Table III of KV were used. The changes in position and width are accurately given in Table II. The asymmetry, with the higher peak being on the high frequency side of ν_0 , is characteristic of both the experimental and calculated curves.

ration occurring is just

$$P_s^1(c) = (1-c)^{\sum_{i=1}^s n_i} c (1-c)^{n_{s+1}} (1-c)^{n_{s+1}} \\ = n_s c (1-c)^{\sum_{i=1}^s n_i + 1}. \quad (5)$$

Configurations of Type II have a probability

$$P_s^*(c) = f^{2s-1} (1-f^{n_s}) - P_s^1(c), \quad (6)$$

where c is the bulk atomic fraction solute, $f = (1-c)$, n_s is the number of lattice sites in the s th shell, and $\sum_s = \sum_{i=1}^s n_i$, the total number of atoms out to and including the s th shell. The probability of Type II occurring is seen to be just the probability (again with only copper atoms inside of shell s) of one or more solutes in the s shell and anything in the $s+1$, minus the probability of one in the s and none in the $s+1$. Two configurations are handled differently; for the tenth shell we use simply $P_{10}(c) = f^{20} (1-f^{n_{10}}) =$ probability of one or more atoms in the tenth shell, and anything beyond. For the probability that there are no solute atoms in all ten shells we have $P_{10}^0 = f^{20}$. In the face-centered cubic lattice, the numbers n_1 through n_{10} have the values, 12, 6, 24, 12, 24, 8, 48, 6, 36, and 24, respectively. The \sum_s are accordingly 12, 18, 42, 54, 78, 86, 134, 140, 176, and 200.

The absorption distribution $I_s^*(\mu)$ was arrived at only after considerable deliberation and represents what is thought to be a reasonable approximation to the actual distribution in the majority of cases. It is a constant over the region $-20/9\alpha\beta$ to $5/4\alpha\beta$, i.e., a region $5/4$ broader than the associated $I_s^1(\mu)$. Various other more involved distributions were considered but were discarded as being unnecessarily complex. The averaging in of lower than axial symmetries should tend to produce a uniform distribution; also it should be noted that the peaks of $I_s^1(\mu)$ are in fact responsible for a relatively small amount of absorption and drop abruptly if smeared. Both $I_s^1(\mu)$ and $I_s^*(\mu)$ are nor-

malized so that

$$\int_{-\nu_0}^{\infty} I_s^1(\mu) d\mu = 1 \quad \text{and} \quad \int_{-\nu_0}^{\infty} I_s^*(\mu) d\mu = 1.$$

A digital computer was used to obtain the products $I_s^1(\mu)P_s^1(c)$, $I_s^*(\mu)P_s^*(c)$, $I_{10}(\mu)P_{10}(c)$, and $I_{10}^0P_{10}^0(c)$ at 100 cps intervals over a 100-kc/sec wide region of the frequency spectrum extending from $\nu_0 - 64 \times 10^3$ to $\nu_0 + 36 \times 10^3$. These individual contributions were summed to give the absorption spectrum

$$I'(\mu, c) = \sum_s [I_s^1(\mu)P_s^1(c) + I_s^*(\mu)P_s^*(c)] \\ + I_{10}(\mu)P_{10}(c) + I_{10}^0P_{10}^0(c) \quad (7)$$

the summation extending from $s=1$ to 9. Special care was exercised to assure the normalization of the functions I_s ; exact integrals were used to evaluate the areas of the peaks of I_s^1 , and the total intensity $P_s^1(c) + P_s^*(c)$ was taken to lie at $\mu=0$ for all cases in which $A_s/h < 200$ cps, and for I_{10}^0 . The function $I_{10}(\mu)$ was of the form I_s^* , i.e., rectangular, normalized, and of width $(5/4)(25A_{10}/9h)$, unless $A_{10}/h < 200$. Except in the cases when some of the absorption falls outside of the region being considered (viz., when $A/h > 36$ kc/sec), we have the check

$$\int_{-\nu_0}^{\infty} I'(\mu, c) d\mu = 1.$$

Accumulated computational errors at this step never exceeded 0.03%. The effect of dipolar broadening was introduced using the Gaussian shape $\exp[-\mu^2/2\sigma^2]$ with $\sigma = 3.6$ kc/sec to approximate the line shape of unalloyed copper. Both

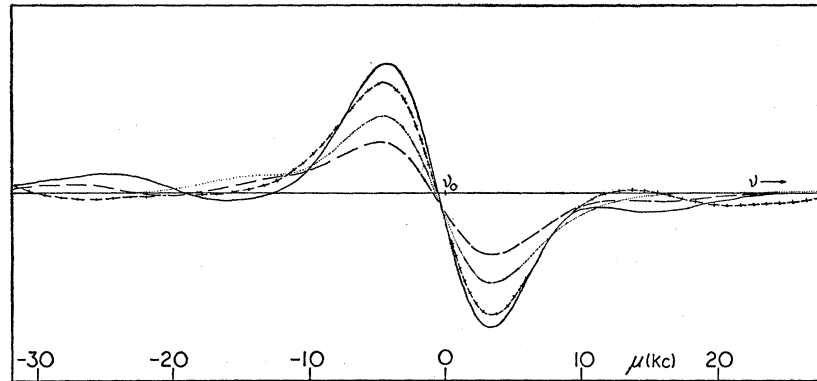
$$I(\mu, c) = \int_{-\nu_0}^{\infty} I'(\mu', c) \exp[-(\mu' - \mu)^2/2\sigma^2] d\mu'$$

TABLE II. Calculated and experimental values of some line shifts $\nu_a - \nu_0$, and line widths $\Delta\nu_{ms}$ (peak to peak, derivative) at $\nu_0 = 4$ Mc/sec.

Composition	$(\nu_a - \nu_0)$ (cps)		$\Delta\nu_{ms}$ (kc/sec)	
	Calc.	Expt.	Calc.	Expt.
Pure Cu	0	0	7.20	7.20 ± 0.05
Zn 0.01	-276		7.58	
0.02	-474		7.99	
0.04	-816		9.02	
0.06	-1190	-587 ± 150	10.08	6.53 ± 0.20
Ga 0.02	-508		7.88	
0.03	-645		8.27	
0.04 ^a	-784	-932 ± 250	8.77	7.95 ± 0.30
Ge 0.01	-513	-356 ± 150	7.89	6.76 ± 0.20
0.02	-754		8.14	
0.03	-883		8.08	
0.04	-1028	-773 ± 300	7.95	6.82 ± 0.40
As 0.01	-774	-335 ± 100	8.52	7.10 ± 0.20
0.02	-1270		9.50	

^a The experimental values apply to a 0.045 atomic fraction Ga alloy.

Fig. 9. Computed absorption derivative curves for a Cu-2 at. % Ge alloy at $\nu_0=12, 8, 4,$ and 2 Mc/sec in order of decreasing amplitude. Side structures are smeared out in the real alloy and are noticeable only as extended tails.



and $dI/d\mu$ were computed, the latter in order to facilitate comparison with experiment. The experimental quantity I is to be compared with $I_d = (dI/d\mu)_{\max} - (dI/d\mu)_{\min}$, the computed peak-to-peak height of the derivative. Use of the q_s given in Table III of KV was found to lead to intensities somewhat larger than those found experimentally. Agreement was attained by increasing the q_s values by a factor of 1.1 to 1.5, depending on the solute element as will be discussed in the next section.

The calculations were carried out for $\nu_0 = 4 \times 10^6$ sec^{-1} for several compositions of alloys containing the solutes Cd, Ga, Ge, As, Sb, Ag, and Au. The intensities are best compared with the data graphically and have been plotted in Figs. 1-4 as points. In addition, more extensive calculations were made for 0.01, 0.02, 0.04 at. % Ge and 0.01 at. % As at frequencies ν_0 of 2, 8, and 12 Mc/sec in order to determine whether the frequency dependence was properly understood. A few examples, drawn from the most thoroughly studied systems, will suffice to illustrate the extent of the agreement with experiment as well as specific shortcomings of the model on which the calculations are based. Computed line shapes are shown in Fig. 8 for four Cu-Ge alloys at 4 Mc/sec. As expected, the intensity changes are striking, the line width does not change appreciably, and the derivative curves pass through zero at successively lower frequencies ν_a . Table II gives the calculated position of the derivative zeros relative to ν_0 for this and other systems. The change is not always linear with composition and, in fact, $\nu_a - \nu_0$ does not vary in the same way for every solute. It is monotonically decreasing with c in every case. Returning to Fig. 8, the plateaus appearing on the sides (more noticeably on the low-frequency side, in this case) are caused by a particular relatively populous group of neighbors ($s=5, n_s=24$) for which $A/h=7.17$ kc/sec. The progress of this detail can be followed in Fig. 9 where it is seen to be responsible for the wiggle near -22 kc/sec at $\nu_0=2$ Mc/sec, and is completely lost in the central peak at $\nu_0=12$ Mc/sec. Third neighbors are responsible for the conspicuous bumps in the 12 Mc/sec line. And so the intensity grows.

V. COMPARISON OF THEORY AND EXPERIMENT

The qualitative results of the experimental work have been shown to demand rather definite properties of any suitable theory, specifically that it predict an electric gradient proportional to the excess valence Z' of the solute, and that it decrease about as $1/r^3$ with distance from a solute atom. Before even inserting the theoretical values for q_s [see Eq. (2.29) and Table II of KV] it is clear that they satisfy these criteria. It remains to show that the conduction electron redistribution can produce gradients of the requisite magnitude, and to make the detailed quantitative comparison of the experimental and computed absorption spectra.

Considering first the variation of intensity with solute concentration we find excellent agreement with the theory for the cases $Z'=1, 2$ with somewhat poorer agreement for $Z'=3, 4$ because of the upward curvature of the calculated I_d vs c curves in the latter cases. The exaggerated intensity at high solute concentration appears to be the result of neglecting solutes beyond the $s+1$ shell when considering solutes in the s shell. The spatial oscillation of the electron density (and thus q_s) introduces the complication that $q_{>(s+1)}$ is not necessarily smaller than q_s ; also q_{s+1} may be greater than q_s in which case the function chosen for I_s^* is probably too narrow. Although these exceptions are infrequent, because generally $q(r) \propto 1/r^3$, both do occur for $Z'=3, 4$, as perusal of Table III of KV will show. In every such case [e.g., the 4th neighbors of Ge or the 2nd neighbors of As, both of which happen to be near nodes of $q(r)$] the I_d vs c curve is markedly straightened when appropriate corrections are made. For Cu-Ge, for example, if $n_5 c P_4^*$ is subtracted from every calculated intensity (based on values of q_s only about 6% larger than those derived by Kohn and Vosko) the agreement with experiment is excellent. It may be of interest that the data for Cu-Ge can also be fitted by substituting $q_s = 0.90 \times 10^{23} (r_5/r_s)^3$ where r_s is the distance between the solute and the copper sites in the s shell. Although this straight inverse cube dependence on r_s has no theoretical support, it conveys the order of magnitude of the gradients involved quite

simply; also, the assumptions of the line shape calculation are plainly suited to it.

The curvatures in the calculated I_d vs c curves change markedly with frequency because the relevant atomic configurations change. This makes the precise adjustment of q_s by a multiplicative factor very tedious and probably not highly significant since at least a part of the apparently complex behavior is contributed by the model used for the line shape calculation. Under the circumstances, comparison of the computed and experimental I vs c for each binary system does not seem justified; they will be commented upon by groups with emphasis on the magnitude of q_s required to achieve agreement with experiment.

For the Group II elements, the q used for the line shape calculations (we refer to the values in Table III of KV) are the same for the three solutes. There is good agreement for Zn, somewhat worse for Mg, and for Cd the q_s of KV must be increased by a factor of 1.5 to bring about agreement with experiment. Group III, IV, and V solutes have relatively minor variations in q_s within each group, but we find that although in every case except Cu-Mg the experimental data indicate higher q_s for higher atomic number, the theoretical q_s are more erratic. In keeping with their derivation from the resistivities they always show a decrease from the fourth to the fifth period element so that we can expect consistent disagreement here. In Group III, gradients of 1.5 times the semiempirical KV values were used to obtain the points shown in Fig. 2 for Ga, a greater factor was required for the In and, although no calculations were made, the Al data would require a factor of only about 1.3. The pattern is similar for Group IV solutes; extensive calculations were made only for Ge. In Fig. 2, the circles show the computed intensities corrected for the broadening of I_4^* by 5th shell solutes as discussed above. The input q_s were only 1.06 times the values given by Kohn and Vosko. Comparable results were obtained for the Group V solutes, the KV values for q_s appeared to be approximately 10 to 20% low. In all, the agreement is remarkably good; the semiempirical gradients appear to be consistently low and definitely better for solutes of high Z' . This suggests a gradual overwhelming of possible size effects, which could quite conceivably affect the results.

Referring to Table I, make the hypothesis that local lattice strains can be measured directly by $(1/a)(da/dc)$, and that an atom whose $(1/a)(da/dc)$ is about 0.1 causes an electric gradient (from lattice strain only) comparable to that generated by an atom with no misfit but a $Z'=1$. To be specific, let us say $q=60(1/a)(da/dc)/r^3$. We then find that the gradients in Mg and Cd alloys are largely the result of lattice distortion while for Zn the distortion is unimportant. For solutes of $Z'=2$, the $(1/a)(da/dc)$ would have to exceed 0.2 to become significant; it does this only for In. Continuing to $Z'=3, 4$ we find that in no other case should the size be as important, although the effect is

always in the right direction to cause the systematic (except Mg) increase of n within each valence group. To properly develop this hypothesis, we would have to go back and consider each shell separately; the effect is again to improve the agreement with theory by knocking out the contributions of copper near the solute which happen to experience small gradients by virtue only of being near nodes of $q(r)$. The argument can be successfully extended to Cu-Ag, but not particularly so to Cu-Au. The large ionic core of Au may deform the outer shells of copper and yet not produce atomic displacement [and thus $(1/a)(da/dc)$]. Interestingly, it gives rise to both a residual resistivity and lattice expansion near those for Mg.

Assuming the gradients as found experimentally and as reflected in n are at least as good a measure of the strength of the solute potential as the resistivity, we might well ask whether large lattice distortion is not correlated with diminished resistivity, the lattice distortion somehow partially compensating for the scattering from the "electric" potential only. A glance at the columns $(\Delta\rho/c)$ and $(1/a)(da/dc)$ of Table I definitely encourages this view, which has been expressed by Blatt²² in his use of the solute cell expansion concept in trying to improve the agreement between theoretical and experimental resistivities. In the present context, the disturbing systematic deviation within each group between experiment and the results of Kohn and Vosko might thus be explained.

The experimental variation of intensity with frequency was determined in several ways, as described in Sec. II. Using Cu-Ge and Cu-Sn alloys of several compositions, the change of n with ν_0 was obtained from Figs. 5 and 6. Were q simply proportional to r^{-3} and the metal a continuum of atomic density d so that $n=(4/3)\pi(r_{\text{crit}})^3d$, then it would be expected that $n \propto 1/\nu_0^3$. Here r_{crit} denotes the critical distance from a solute atom at which the parameter ν_0/q^2 leads to a splitting A/h which is just equal to one half of the line width, 3.6 kc/sec for Cu. The intensity of a particular composition sample should accordingly vary with

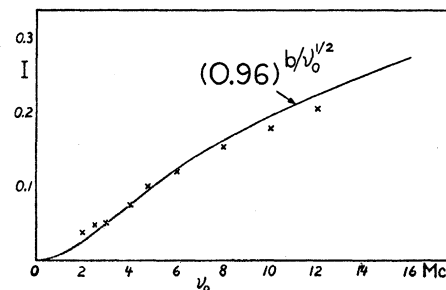


FIG. 10. Measured intensity at several frequencies using mixed 325 mesh Al and Cu-4 at. % Ge powders. The full line corresponds to $b=126 \times 10^8$. Interpretation is simplified because we need consider only one set of $P_s(c)$ rather than many, as a study of n vs ν_0 implies. Similar results were obtained for 1.0 at. % As.

²² F. J. Blatt, Phys. Rev. **108**, 285 (1957).

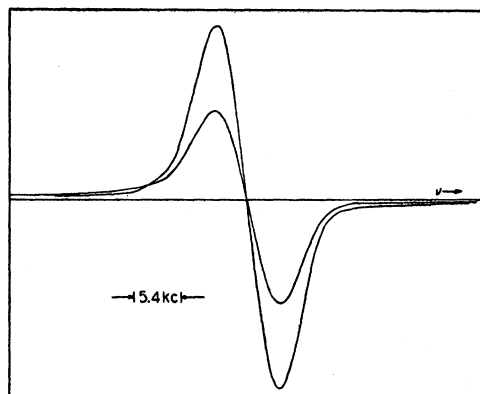


FIG. 11. Experimental resonance absorption derivative curves $\nu_0=2$ Mc/sec for Cu alloys containing 1.0 and 2.0 at. % Ge, the latter corresponding to the smaller curve. Note the extended wings.

frequency as $(1-c)^{b/\nu_0}$. Both of these relationships work well in predicting the change in behavior of intensity with ν_0 . Figure 10 compares the data from a Cu-4 at. % Ge alloy with the foregoing relationship in which $b=126 \times 10^3$. The measurements were made on an intimate mixture of 325 mesh alloy and pure aluminum powders. This relatively crude argument for the frequency dependence of n and I gives better agreement with experiment than the model on which the calculations are based. Attempts to derive the intensity as a function of ν_0 lead to all of the difficulties mentioned during the discussion of adjusting q for best fit. As the parameter $p = \nu_0/q^2$ is changed, the fine (shell) structure emphasized by our model introduces uneven changes in the intensity which therefore oscillates around the smooth dependence upon p which results from the above cruder picture. Very careful extended runs at several frequencies were made in which the absorption was recorded over a region at least eight line widths wide. Close scrutiny failed to reveal any side "lines" (of the type shown in Fig. 9), bumps, or plateaus. The intensity appears just to grow smoothly with increasing frequency although the factor of 6 change in ν_0 (2 to 12 Mc/sec) was not large enough to confirm the presence or absence of a shell structure of the type inherent to our model. These experiments were done after the calculations were complete enough so that the most extreme situations of predicted irregularities in line shape could be investigated. Only a slight broadening and asymmetry were ever noted. Figures 11 and 12 illustrate this point; each is a composite of at least four passes through the absorption using a slow sweep rate (13 gauss/hour), and marginal oscillator. It is clear that the side lines and much of the irregularity in the growth of the intensity with increasing ν_0 are artificialities introduced by our model. The excessively large calculated values of line shift and width given in Table II can be similarly rationalized. Even though

only some 10–15% broadening is predicted, the observed value is much less.

A phenomenon resembling base line drift can be discerned in many of the experimental curves, and somewhat less clearly in Figs. 8 and 9. It is caused by the sizable diffuse absorption distributed over a wide (≈ 200 kc/sec) region around ν_0 . Unfortunately this gentle decrease in absorption occurs over such a large region, and so slowly, that it is not possible from the present measurements even to obtain a useful estimate of its shape or second moment. In this regard it may be noted that we have made no use either of calculated or measured moments. It was felt that the extensive frequency distribution of the absorption coupled with the peculiar and partially uncertain line shapes (Fig. 7) severely limited the usefulness of a moment analysis. The best that could have been done would have been to truncate the curves at some point and estimate their second moments. This approach would lead to approximately the same moment in every case for the present alloys.

For the primary purpose of comparing the line shape calculation described above with that used by Seymour,²³ we calculated the absorption lines and I vs c dependence of Cu-Ni at 3.0 and 7.0 Mc/sec using the gradient put forth by him. The computed intensities fell very near a straight line of slope 20.8 for $\nu_0=3.0$ Mc/sec rather than 28 as required by Seymour's data, indicating that the present method of computation evolves intensities rather larger than his, given the same input $q(r)$. The data on Ni presented in Fig. 4 were obtained prior to our knowledge of Seymour's work, but are in complete agreement with his findings. Although we hesitate on the basis of the present work to cross the boundary represented by the noble metals, the results of this investigation indicate that the electric gradient surrounding Ni atoms may also originate in a conduction electron redistribution. As Seymour observes, it is not likely that gradients around Ni are caused by atomic size differences. The n found for Ni

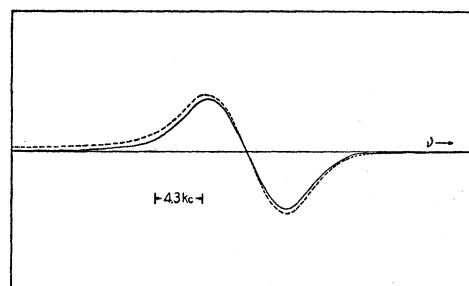


FIG. 12. Experimental absorption derivatives obtained at 4.0 Mc/sec for Cu alloys with 1.5 at. % Ga (dashed) and 1.0 at. % As. As in Fig. 11, the tails approach the axis smoothly with no structure apparent.

²³ A. C. Chapman and E. F. W. Seymour, Proc. Phys. Soc. (London) **72**, 797 (1958).

agrees with that for Group II elements and suggests a charge of unity for it. We would assume, of course, that $Z' = -1$ but the experiments are insensitive to the sign of Z' .

Every major feature of the experiments has been explained by using the gradients given by KV. Divergences of theory and experiment are traceable to the model used for the line shape calculation in every case and therefore are not significant except to point the way for an improved model. The impetus to provide same is lacking at present because in no case was it possible experimentally to detect or identify specific component lines arising from known shells. It was hoped that the study of I vs ν_0 , for instance, might have allowed a definite conclusion regarding the spatial distribution of $q(r)$. Lacking this, we are unable to check the details of the q_s put forth by KV and must be content for now to state that although any gradient roughly proportional to Z'/r^3 and of suitable magnitude will explain the observations, the only rigorous theoretical calculations which at present provide the necessary gradient are those of KV which stem from

Friedel's observation that a self consistent treatment of the charge around a solute atom reveals a variation in charge density created at a large distance from the dissolved atom. The importance of this interesting "second term" which appeared in Friedel's earlier electron density calculations seems to be more clearly emphasized by experiments of the type described here than any other currently in use.

ACKNOWLEDGMENTS

The interest expressed in this work by Professor Kohn and Professor Vosko has been a source of encouragement for which I am very grateful. It is a pleasure also to thank Professor J. Friedel and his group, particularly E. Daniel and A. Blandin, for their continuing interest and correspondence on the topic of the long-range oscillations. The assistance of Mr. J. R. Radecki with the experiments, and of Mr. E. P. Muth with the calculations was of great help in hastening the completion of this investigation. We are indebted to the U. S. Atomic Energy Commission for support during the latter part of this work.

Theory of Nuclear Resonance Intensity in Dilute Alloys*†

W. KOHN‡ AND S. H. VOSKO

Carnegie Institute of Technology, Pittsburgh, Pennsylvania

(Received March 18, 1960)

Experiments of Bloembergen and Rowland have shown that the intensity of the nuclear resonance signal in metallic Cu decreases rapidly when small quantities of other elements are alloyed with it. These results require that each solute atom produces significant electric field gradients in its vicinity, sometimes affecting as many as 85 neighboring Cu nuclei. In this paper we show that field gradients of approximately the required magnitude arise from the redistribution of the conduction electron charge density near the solute atoms. A crucial feature of our theory is that at large distances r from a solute atom the electron density behaves as $\cos(2k^0r + \varphi)/r^3$ where k^0 is the Fermi wave number and φ is a phase. Our agreement with experiment is a confirmation of this behavior. Such an oscillatory behavior is a consequence of a discontinuous drop at the Fermi surface of $n(\mathbf{k})$, the occupation probability of the conduction band function with wave vector \mathbf{k} .

1. INTRODUCTION

BLOEMBERGEN and Rowland¹ and Rowland² have observed that the nuclear resonance signal in metallic copper decreases rapidly when small amounts of solute are introduced. These measurements require for their explanation that the solute atoms give rise to substantial field gradients which act on the Cu nuclear quadrupole moments as far as the sixth and seventh nearest neighbors. Two possible mechanisms

suggest themselves as responsible for this effect. One is that the field gradients are associated with the strain around the solute atoms, which does indeed fall off slowly, namely as r^{-3} . However as one finds only minor correlation between the strains expected around different solutes and their effectiveness in reducing the resonance signal, this explanation is not satisfactory. Another possibility is that the field gradients arise from the electron charge which screens the solute atoms. This is supported by the strong correlation of the measured effects with the valence difference between the solute and copper. However if the screening is described by an exponentially decreasing electron charge density of the Thomas-Fermi type, the associated

* Supported in part by the Office of Naval Research.

† A preliminary account was published in *Bull. Am. Phys. Soc.* **5**, 176 (1960).

‡ Present address: Department of Physics, University of California, La Jolla, California.

¹ N. Bloembergen and T. J. Rowland, *Acta Met.* **1**, 731 (1953).

² T. J. Rowland, preceding paper [*Phys. Rev.* **119**, 900 (1960)].