

Contribution of Strain to Nuclear Quadrupole Interactions in Dilute Alloys of Copper

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The hypothesis that electric field gradients due to elastic strains (size effect) about the solute atom in dilute alloys of a cubic metal form an important part of the total field gradient at the solvent nuclei is developed quantitatively. Results have been applied to a consideration of recent nuclear magnetic resonance experiments by Rowland on dilute copper alloys which were interpreted by him and by Kohn and Vosko in terms of the spatially oscillating charge due to conduction electron redistribution (valence effect.) The good agreement with theory they obtained is further improved to a significant degree by the simultaneous consideration of both size effect and valence effect. It is found that the field gradients due to size effect are in fact comparable in magnitude to those due to the valence effect. The magnitude of the size effect is described by a single parameter characteristic of the solvent. It is found that the value of this parameter obtained for copper metal is larger than that indicated by recent experiments by Faulkner and by Averbuch, de Bergevin, and Müller-Warmuth, and possible causes of this disagreement are discussed.

I. INTRODUCTION

EARLY work of Bloembergen and Rowland¹ showed that small amounts of substitutional diamagnetic impurities in copper and aluminum cause a considerable decrease in the intensity of the nuclear magnetic resonance (NMR) absorption line of the solvent metal. Recent data of Rowland² have shown that the intensity decrease in copper requires an interaction extending as far as the seventh-nearest-neighbor shell to a high-valence impurity such as antimony. It was already realized at the time of the earlier experiments¹ that the decrease of intensity was due to second order electric-quadrupole interactions, but the origin of the necessarily large electric-field gradients was not even qualitatively understood until quite recently. One possible source of electric field gradients in the alloy is the lattice strain caused by the impurity (size effect). These gradients can be estimated from tabulated atomic radii for the impurities or by use of experimental lattice-parameter data, but the NMR data obtained by Rowland on a wide variety of impurities in copper enabled him² to rule decisively against a theory³ based on size effects alone. A second possible source of electric-field gradients is the excess charge of the diamagnetic impurity reduced by the screening due to the conduction electrons (valence or charge effect). However, the early calculation¹ of the electric field gradient produced this way was based on the Thomas-Fermi model and predicted an interaction which is too small to explain the experimental results. On the other hand, Rowland² obtained a marked correlation in his results with the valence group to which the solute belongs and found in fact an indication that the field gradients vary approximately with the inverse cube of the distance to the impurity. Confirmation of his hypothesis that the field gradients were due to

valence effect came from calculations⁴⁻⁷ which indicated that there are long-range oscillations of the charge density of the screening conduction electrons around an impurity atom which are not predicted by the Thomas-Fermi model. The electric-field gradients produced by these charge oscillations have been used^{2,7} successfully to explain the main features of Rowland's data. Rowland's conclusion was that the origin of electric gradients around multivalent solutes in copper is almost purely an effect of conduction electron distribution and that the inhomogeneous strains introduced by solutes had a relatively slight influence on the gradients in most of the alloys investigated. He recognized however that deviations from the behavior predicted by the charge distributions of KV appeared to be in the right direction to be ascribed to lattice strains. The assumption that the valence effect is overwhelming and the strain effect is slight also enters into the work of Blandin and Friedel⁸ who mention that the stimulus to their treatment of quadrupole effects in alloys in terms of long-range oscillating-charge effect arose from the experimental result of Averbuch *et al.*⁹ indicating that the strain-induced field gradients were small.

In the present paper, the effect of strain-induced electric-field gradients *in addition* to the valence or charge effect has been considered in detail and it has been found that this use of both size and valence effect can quantitatively explain many of the discrepancies between the experimental results in copper and the charge-only theory. Furthermore, it appears from the

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

² T. J. Rowland, *Phys. Rev.* **119**, 900 (1960). We wish to thank Dr. Rowland for a prepublication copy of his paper.

³ N. Bloembergen, Report of Conference on *Defects in Crystalline Solids*, Bristol, 1954 (The Physical Society, London, 1955) p. 1.

⁴ J. Friedel, *Phil. Mag.* **43**, 153 (1952); *Suppl. Nuovo cimento* **2**, 287 (1958).

⁵ A. Blandin, E. Daniel, and J. Friedel, *Phil. Mag.* **4**, 180 (1959); *J. Phys. Chem. Solids* **10**, 126 (1959); E. Daniel, *J. phys. radium* **20**, 51 (1959); **20**, 849 (1959).

⁶ J. S. Langer and S. H. Vosko, *J. Phys. Chem. Solids* **12**, 196 (1959).

⁷ W. Kohn and S. H. Vosko, *Phys. Rev.* **119**, 912 (1960) (referred to in the text as KV).

⁸ A. Blandin and J. Friedel, *J. Phys. Chem. Solids*, **17**, 170 (1960), *J. phys. radium* **21**, 689 (1960).

⁹ P. Averbuch, F. de Bergevin, and W. Müller-Warmuth, *Compt. rend.* **249**, 2315 (1959).

present results that the field gradients associated with size effects are in general *not negligible* but are in fact of the same order of magnitude as those associated with valence effects.

In Sec. II of this paper we describe how, given the field gradients at the different lattice sites, one can compute "wipeout numbers" for direct comparison with Rowland's data for copper. In Sec. III the origin of the field gradients is discussed. For the charge contribution we take the KV theory, but regard the enhancement factor α as an adjustable empirical parameter within their estimated theoretical limits of error. The size effect is similarly described with the aid of a single adjustable dimensionless parameter λ . We then show how size and valence effects are combined and the parameters α and λ adjusted for optimum fit with experimental data. The numerical results are presented in Sec. IV and the apparent discrepancy between our determination of the stress-induced field gradients and the work of Averbuch *et al.*⁹ and Faulkner^{10,11} is discussed. Our conclusions are summarized in Sec. V.

II. CALCULATION OF WIPEOUT NUMBERS

Our discussion will be confined to the dilute alloys of copper where the extensive data of Rowland² make significant calculations possible. Both of the copper isotopes, 63 and 65, have nuclear spin $I = \frac{3}{2}$ and approximately the same magnetic dipole moment and nuclear electric quadrupole moment. Rowland's experiments made use of the signal from the more abundant Cu⁶³.

Cohen and Reif¹² have given an extensive survey of the theory of quadrupole interactions in solids. We will summarize those results which are pertinent to the present investigation.

In an external magnetic field, a spin $\frac{3}{2}$ system splits up into 4 equally-spaced energy levels, with three transitions of the same frequency satisfying the selection rule $\Delta m = \pm 1$. In a pure metal of perfect cubic symmetry, there is zero nuclear quadrupole interaction. If an impurity is introduced into the metal, the cubic symmetry at the nearby lattice sites is destroyed, a nonzero electric field gradient will appear at these sites, and the nuclear resonance absorption will be perturbed by the resulting quadrupole interaction. If the shift in the frequency of the "satellite" lines ($m = \frac{3}{2} \rightarrow \frac{1}{2}$ and $m = -\frac{1}{2} \rightarrow -\frac{3}{2}$) due to quadrupole interactions is calculated by perturbation theory, a shift is found in first order. Thus the satellite lines are affected by relatively small perturbations and it has been found experimentally, in fact, that the satellites in copper are sensitive even to imperfections such as dislocations.³ The "central" line ($m = \frac{1}{2} \rightarrow -\frac{1}{2}$) is not shifted in first order but is shifted in second order. Experimentally the

central line appears to be unaffected by dislocations. For this reason, the central line provides a more convenient tool for the study of impurities since it is not necessary to take great care in annealing. All of Rowland's data on copper alloys refer to the central line, since the concentration of impurities he used (0.5% up) was sufficient to annihilate any contribution by the satellite lines to the intensity of the observed resonance absorption.

The calculation of quadrupole interactions is greatly simplified by assuming axial symmetry for the electric field gradient seen by the copper nucleus being resonated. For the valence effect, this assumption is consistent with the approximation made in computation⁷ of the screened charge around an impurity which results in spherically-symmetric screening. For the size effect, the degree of validity of the axial symmetry approximation is less certain and will be discussed below.

On the assumption of axial symmetry, the shift in the frequency of the central transition of a spin $\frac{3}{2}$ system in second-order perturbation theory, measured from the unperturbed resonant frequency, is given by

$$\nu - \nu' = -A(1 - \cos^2\theta)(9 \cos^2\theta - 1), \quad (1)$$

where ν is the $\frac{1}{2} \rightarrow -\frac{1}{2}$ transition frequency in the presence of the perturbation, ν' is the resonant frequency of the unperturbed nucleus in the external field, $A = (a - \frac{3}{4})\nu_Q^2/16\nu$, $\nu_Q = 3e^2qQ/2I(2I-1)\hbar = -0.273 \times 10^{-17}q$ cps for ¹³Cu⁶³, $a = I(I+1)$, θ is the angle between the external magnetic field and the radius vector from the impurity to the copper atom in question, and $q = (1/e)(\partial^2 V/\partial z^2 - \nabla^2 V/3)$, where V is the electrostatic potential, and z is the axis of symmetry.

Equation (1) gives the quadrupole interaction frequency shift for a given q and given θ . In the actual alloy, the frequency shift will vary from lattice point to lattice point for two reasons: (1) q , and hence A , varies with distance from the impurity atom, and (2) θ is in general different for different lattice points, even in a single crystal. Since powdered samples are used in resonance experiments in metals, there will be a random distribution of θ in Eq. (1). This leads, for a given value of A , to an easily derivable frequency spectrum, which we shall denote by $p(\nu - \nu', k)$, where $k = A/\Delta\nu$ and $\Delta\nu$ is a constant to be defined below. [The expression for this frequency spectrum is given in Eq. (9.7) in Cohen and Reif.¹²] Thus in a powder, a nucleus resonating at ν' in the absence of second-order quadrupole perturbation will have a frequency spectrum $p(\nu - \nu', k)$ in the presence of the perturbation. In pure copper where there is no quadrupole interaction, $k = A = 0$, and the linewidth is due primarily to dipole-dipole interaction. We shall denote the absorption line shape of pure copper

¹⁰ E. A. Faulkner, *Nature* **184**, 442 (1959).

¹¹ E. A. Faulkner, *Phil. Mag.* **5**, 843 (1960).

¹² M. N. Cohen and F. Reif, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 5, p. 321.

¹³ For numerical work we have used $Q(\text{Cu}^{63}) = -0.157 \times 10^{-24}$ cm², following Rowland.² This value, stated to be uncorrected for Sternheimer polarization, was obtained by B. Bleaney, K. D. Bowers, and M. H. L. Pryce, *Proc. Roy. Soc. (London)* **A228**, 166 (1955).

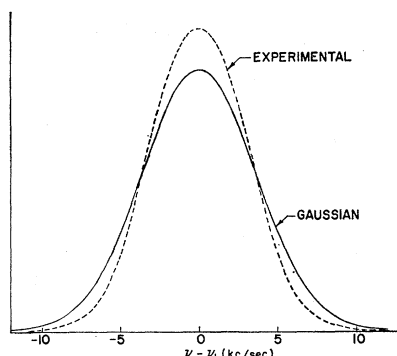


FIG. 1. Experimental NMR absorption curve for high-purity, well-annealed copper, compared with a Gaussian curve of the same half-width and area.

by $g(\nu, 0)$. We then make the assumption that in the presence of the quadrupole interaction the resultant line shape, $g(\nu, k)$, for a given value of k , can be obtained by "folding" the quadrupole line shape, $p(\nu - \nu', k)$ into the unperturbed line shape, $g(\nu, 0)$:

$$g(\nu, k) = \int_0^\infty g(\nu', 0) p(\nu - \nu', k) d\nu'. \quad (2)$$

An experimental absorption line for a well-annealed sample of high-purity copper¹⁴ is shown in Fig. 1, along with a Gaussian curve for comparison. Both curves have unit area, and the linewidth (defined as the full width between points of maximum slope) of the Gaussian has been set equal to that of the experimental curve (7.2 kc/sec). The area contained in the tails of the Gaussian, beyond the region where the experimental curve becomes zero, is negligible. It is tempting to use the Gaussian for $g(\nu, 0)$ since the use of an analytic function greatly simplifies the computing problem. However, the experimental curve is considerably sharper. The ratio of the linewidth to the square root of the second moment for the experimental curve is 2.4, which differs appreciably from the value 2 for the Gaussian. A preliminary calculation indicated that in some cases our calculated results might be quite sensitive to the shape of the unperturbed line near the center. For these reasons we used the experimental curve for $g(\nu, 0)$. It turned out however that our final results would have been almost unchanged had the Gaussian been used. Because Rowland's copper alloy experimental data was presented in terms of the variation with impurity concentration of the peak-to-peak height of the *derivative* of the absorption curve, we actually compute $dg(\nu, k)/d\nu$ rather than $g(\nu, k)$, and do this directly by replacing $g(\nu', 0)$ in Eq. (2) by $dg(\nu', 0)/d\nu'$. The results of this folding operation are shown in Fig. 2, where $dg(\nu, k)/d\nu$ is plotted vs frequency for several values of k . $\Delta\nu$ in the definition $k = A/\Delta\nu$ is taken to be

the frequency width between the peaks of the experimental derivative curve for pure copper (labeled $k=0$ in Fig. 2).

The resultant calculated derivative line shape for the entire alloy sample, $dG(\nu)/d\nu$, is found by summing over all lattice sites in the sample

$$dG(\nu)/d\nu = \sum_i dg(\nu, k_i)/d\nu, \quad (3)$$

where k_i is the value of the quadrupole interaction constant at the i th lattice site, determined by the value of the electric field gradient q at this site. The origin and calculation of q will be discussed below.

A convenient method of comparing theoretical calculations of intensity vs impurity concentration with the experimental results is to compare so-called "wipeout numbers." The wipeout number, W , per impurity atom for an alloy sample with a given impurity concentration is defined as the difference between the number of copper atoms in the alloy sample and that number of atoms in a pure copper sample required to give the same intensity in the central line, divided by the number of impurity atoms. The electric-field gradient around an isolated impurity must decrease with distance from the impurity, eventually becoming small enough so that for atoms outside a sphere of large enough radius the interaction is too small to affect the intensity of the signal. If the "all or nothing" or "critical sphere" model held, then a copper atom inside the sphere of influence would have its resonant frequency shifted by so large an amount as to be unobservable. In that case the wipeout number would be just equal to n , the number of copper atoms inside the sphere of influence. However, in general, each atom inside will contribute some fraction of its intensity to the resultant line, so that W will be less than n . Let N be the total number of atoms in a sample, and let c be the fractional atomic concentration

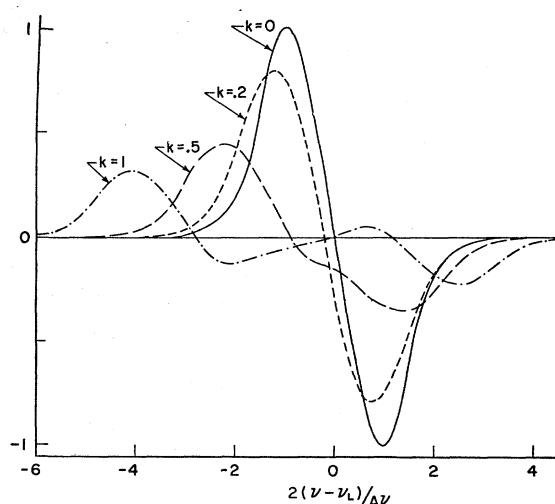


FIG. 2. Theoretical absorption derivative curves, $dg(\nu, k)/d\nu$, for various values of the quadrupole interaction parameter $k = A/\Delta\nu$. $k=0$ corresponds to the unperturbed experimental line of width $\Delta\nu$.

¹⁴ We wish to thank Dr. J. A. Hofmann of our laboratory for the experimental curve.

of impurity. The total number of impurity atoms is then Nc and the total number of copper atoms is $N(1-c)$. For very dilute concentrations where the overlap of the impurity spheres of influence can be neglected, the total number of copper atoms affected by the impurities is nNc . If I_0 is the absorption intensity per copper atom for pure copper and I_i is the absorption intensity of the i th copper atom inside a sphere of influence in the alloy, then the absorption intensity F for the whole alloy sample is

$$F = [N(1-c) - nNc]I_0 + cN \sum_{i=1}^n I_i. \quad (4)$$

By definition, the equivalent number of pure solvent atoms for this alloy sample is F/I_0 and the wipeout number per impurity atom is therefore $[N(1-c) - F/I_0]/Nc$, or

$$W = n - \sum_{i=1}^n I_i/I_0 = \sum_{i=1}^n w_i, \quad (5)$$

where w_i , a wipeout fraction for the i th copper atom, is defined by

$$w_i = 1 - I_i/I_0. \quad (6)$$

Since we wish to compare our calculated wipeout numbers with wipeout numbers computed from Rowland's data, we should take for I_i the contribution of the i th atom to the peak-to-peak height of the resultant derivative curve of the alloy sample, that is,

$$I_i = \left| \left(\frac{dg(\nu, k_i)}{d\nu} \right)_{\nu=\nu_{\max}} - \left(\frac{dg(\nu, k_i)}{d\nu} \right)_{\nu=\nu_{\min}} \right|, \quad (7)$$

where ν_{\max} and ν_{\min} are the frequencies at which the two peaks of the $dg(\nu)/d\nu$ occur. This naturally requires knowing ν_{\max} and ν_{\min} , but these frequencies can be determined only by actually calculating a portion of the resultant derivative curve by Eq. (3). A considerable saving in computation may be had by noting that since the slope of the derivative curve is zero at the peaks and since the frequency shift between the peaks of the resulting curve in the alloy and the corresponding peaks in pure copper will be small for low impurity concentration, only a small error will be introduced by taking

$$I_i = \left| \left(\frac{dg(\nu, k_i)}{d\nu} \right)_{\nu=\nu_1} - \left(\frac{dg(\nu, k_i)}{d\nu} \right)_{\nu=\nu_2} \right|, \quad (8)$$

where ν_1 and ν_2 are the frequencies at which the derivative peaks occur in pure copper and are related to the previously defined $\Delta\nu$ by $\Delta\nu = |\nu_1 - \nu_2|$. By definition of I_0 , we take

$$I_0 = \left| \left(\frac{dg(\nu, 0)}{d\nu} \right)_{\nu=\nu_1} - \left(\frac{dg(\nu, 0)}{d\nu} \right)_{\nu=\nu_2} \right|. \quad (9)$$

The two terms in I_0 in Eq. (9) are just the heights of the peaks of the $k=0$ curve in Fig. 2 and for the values

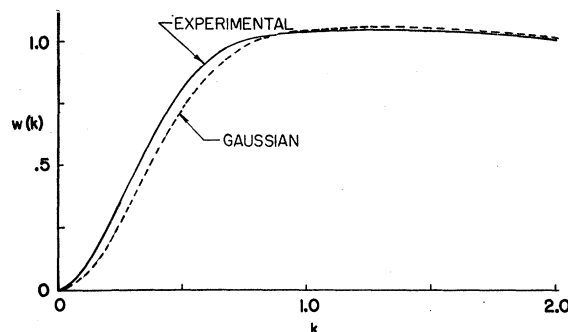


FIG. 3. Theoretical wipeout fraction $w(k)$, as function of the quadrupole interaction parameter $k = A/\Delta\nu$. The solid curve was calculated from the theoretical absorption curves plotted in Fig. 2, which were derived from the experimental absorption curve of the pure metal. The dashed curve was obtained using the Gaussian approximation for the absorption curve of the pure metal.

of k used in Fig. 2, the two factors in I_i in Eq. (8) are the heights of the broken curves at the two frequencies at which the peaks occur for $k=0$. In Fig. 3, $w_i = w_i(k_i)$ is plotted as a function of k_i , using Eqs. (6), (8), and (9).

The calculation of a wipeout number, W , consists of the following steps: For the impurity in question, the value of q for the i th lattice point is chosen as discussed in the next section. This determines A_i , and so determines $k_i = A_i/\Delta\nu$. From Fig. 3, we read off $w_i(k_i)$, and then compute $W = \sum_i w_i$.

If, as will be assumed in the next section, the electric-field gradient q is a function only of the distance to the nearest impurity, we may sum over shells of atoms at a given distance from the impurity and we may then calculate W from $W = \sum_s n_s w_s$, where n_s is the number of atoms in the s th nearest neighbor shell and $w_s = 1 - I_s/I_0$.

III. ORIGIN OF THE FIELD GRADIENTS

We will make the assumption that the resultant electric field gradient at the solvent atom sites of a dilute alloy of cubic structure has its origin in two independent effects. The impurity will scatter the conduction electrons because of its excess charge or differing electronic structure. The resultant redistribution of conduction electron charge will lead to electric field gradients which we have called the *valence* or *charge effect*. In addition, the size difference between impurity and solvent atoms will cause a distortion which will destroy the cubic symmetry of the lattice when viewed from the solvent atom sites. The resulting electric field gradient is the *size effect*.

Valence Effect

As previously mentioned, recent theoretical work⁴⁻⁷ has indicated the presence of long-range oscillations in the screening charge density around a diamagnetic impurity in a metal. Langer and Vosko,⁵ Takimoto,¹⁵ and

¹⁵ N. Takimoto, J. Phys. Soc. Japan 14, 1142 (1959); see also R. J. Harrison and A. Paskin, *ibid.* 15, 1042 (1960).

Silverman and Weiss,¹⁶ independently applied various types of many-body theory to the spin-independent impurity screening problem. These calculations provide an analytical expression for the Fourier components of the self-consistent potential, but the potential itself and the associated self-consistent, total charge density can be obtained analytically only in the approximation equivalent to the Thomas-Fermi method. Of these authors, only Langer and Vosko pointed out that the asymptotic expression for the potential has an oscillating component, similar to that given by Friedel,⁴ in contrast to the monotonic exponential decrease of the Thomas-Fermi solution. They also numerically integrated the general expression for the charge density and pointed out the consequent long-range oscillation in the electric field gradient.

The many-body calculations cited assume a free electron gas and are not strictly applicable to real metals. Most serious, as pointed out by Kohn and Vosko,⁷ is the use of plane waves instead of Bloch waves for the unperturbed wave functions, since the magnitude of the quadrupole effect is strongly dependent upon the value of the wave function near the nucleus. For this reason KV used ordinary one-particle scattering theory for Bloch waves to determine the asymptotic form of the charge density and determined the first two phase shifts by fitting the residual resistivity and the Friedel sum rule.¹⁷ Higher order phase shifts were neglected. Blandin and Friedel⁸ have independently made a less extensive calculation along the same lines as KV. March¹⁸ has also recently considered the screening problem by numerically summing the one-particle wave functions for a finite number of particles in a spherical box, assuming an exponentially screened Coulomb potential for the defect. No mention of the quadrupole interaction problem is made but his charge density is in qualitative agreement with the many-body theories.

Rowland² used the KV results for comparison with his experimental data. For the charge effect we will also use the electric-field gradients calculated by KV except that we will consider the enhancement factor α as one to be determined empirically instead of using the KV theoretical value of 25.6.

Thus, using the notation q_α to denote the charge contribution to q , we have for q_α [from Eq. (2.29) of KV]

$$q_\alpha = \frac{1}{3}\alpha 8\pi A' \cos(2k^0 r + \phi)/r^3, \quad (10)$$

where the values of A' and ϕ are deduced by KV from phase shift analysis of residual resistivity data for copper alloys, k^0 is the momentum at the Fermi surface, assumed spherical, and r is the distance to the impurity. The assumption has been made in the derivation of this expression that the shielding of the impurity charge is

spherically symmetric. Therefore the corresponding field gradient is axially symmetric with respect to the radius vector to the impurity.

Size Effect

To calculate the size effect one must know the strain field and in addition the relationship between strain and the electric-field gradient at the positions of the nuclei contributing to the NMR. The latter relationship for a real metal has not been evaluated theoretically. Instead a phenomenological approach is usually taken and we adopt this approach in the present work. A linear point relationship is assumed between the elastic strain tensor and the electric-field-gradient tensor. Such a point relationship may be expected to be a reasonably good approximation for a metal¹⁹ even in regions of rapidly varying strain in the neighborhood of the impurity because of the relatively strong shielding of electric fields due to distant atoms. This point relationship is expressible in terms of a fourth-order field gradient-strain tensor F_{mn} , where m, n take on the values 1 through 6 in the Voigt notation of elasticity theory.

For a nucleus at a site of cubic symmetry, symmetry arguments²⁰ lead to equalities and zeros among the F_{mn} and it can be shown that the field gradient tensor V_{ij} is given by

$$V_{ij} = \delta_{ij}[(F_{11} - F_{12})\epsilon_{ii} + F_{12} \sum_l \epsilon_{ll}] + (1 - \delta_{ij})2F_{44}\epsilon_{ij}, \quad (11)$$

where i, j, l refer to components in the direction of the three cubic axes. δ_{ij} is the Kronecker delta, and $\epsilon_{ij} = \frac{1}{2}[(\partial u_i/\partial x_j) + (\partial u_j/\partial x_i)]$ is the strain tensor in which u_i, u_j are the components of the displacement of the nucleus located at coordinates x_i . There are then in general three independent components of the F tensor for the case of cubic symmetry. However, the electric quadrupole interaction only involves field gradient combinations of the form

$$V_{ij} - \frac{1}{3}\delta_{ij}\nabla^2 V = (F_{11} - F_{12})\delta_{ij}[\epsilon_{ii} - \frac{1}{3}\sum_l \epsilon_{ll}] + 2(1 - \delta_{ij})F_{44}\epsilon_{ij}, \quad (12)$$

so that for consideration of quadrupole effects only the two quantities $(F_{11} - F_{12})$ and F_{44} are relevant.²¹ These are independent for the general case of cubic symmetry. The general case is complicated since the field gradient quadric does not then have axial symmetry with respect to an arbitrary radius vector through the impurity even when the strain quadric does have this symmetry. To obtain the desired axial symmetry we have found it

¹⁹ See reference 12, p. 364.

²⁰ R. B. Shulman, B. J. Wyluda, and P. W. Anderson, Phys. Rev. **107**, 953 (1957).

²¹ The additional relationship $F_{11} = -2F_{12}$, which is often assumed in the case of cubic symmetry, would not here further reduce the number of relevant parameters. This relationship follows from the requirement, fulfilled only for special models, that there is no change in charge density produced by a general strain field, even one for which the dilatation $\sum_l \epsilon_{ll}$ is not zero.

¹⁶ B. Silverman and P. Weiss, Phys. Rev. **114**, 989 (1959).

¹⁷ J. Friedel, Advances in Phys. **3**, 446 (1954); see also J. S. Langer and V. Ambegaokar, Phys. Rev. **121**, 1090 (1961).

¹⁸ N. March, Proc. Roy. Soc. (London) **A256**, 400 (1960).

expedient to assume an isotropic field-gradient-strain relationship, that is to assume that the principal axes of the field gradient quadric and the strain quadric always coincide. In this case, $F_{44} = \frac{1}{2}(F_{11} - F_{12})$ and Eq. (12) reduces to

$$V_{ij} - \frac{1}{3}\delta_{ij}\nabla^2 V = (F_{11} - F_{12})[\epsilon_{ij} - \frac{1}{3}\delta_{ij}\sum_l \epsilon_{ll}]. \quad (13)$$

Thus the \mathbf{F} tensor has been reduced to the single independent quantity, $F_{11} - F_{12}$. Taylor and Bloembergen²² have actually found an isotropic relationship in experiments on sodium chloride, and Averbuch *et al.*⁹ have suggested that this provides even more reason to assume isotropy for metals. The single phenomenological coefficient ($F_{11} - F_{12}$) cannot at present be computed from first principles. It is convenient to introduce a dimensionless parameter λ to describe the magnitude of ($F_{11} - F_{12}$). Such a parameter was defined by Faulkner¹⁰ with respect to a point-charge model. If one assumes that the field at a given site in a uniformly deformed, face-centered cubic lattice of lattice parameter a is due to unshielded point charges $+e$, at the twelve first neighbor sites, it turns out that $(F_{11} - F_{12}) = 9ed^{-3}$ and $F_{44} = -3ed^{-3}$, where $d = 2^{-\frac{1}{2}}a$ is the nearest neighbor distance. Faulkner then assumed that all F_{mn} for the real metal could be written as λ times the corresponding values for the point charge model. We take Faulkner's definition to apply to $(F_{11} - F_{12})$, but not to F_{44} , since his definition contradicts our assumption of isotropy [i.e., for the point charge model $F_{44} \neq \frac{1}{2}(F_{11} - F_{12})$]. We will therefore define λ for the isotropic case by

$$(F_{11} - F_{12}) = 9ed^{-3}\lambda, \quad (14)$$

and continue to assume that $F_{44} = \frac{1}{2}(F_{11} - F_{12})$. While the condition $\lambda = 1$ does not correspond exactly to the point-charge model, λ may still be regarded as a qualitative measure of the ratio of the field gradient in the real metal to the field gradient deduced from the point-charge model.²³

In order to compute the strain field about an impurity in a metal we take the "misfitting sphere model."²⁴ The assumption is that the metal may be regarded as an isotropic homogeneous elastic continuum. This is consistent with, although independent of, the assumption made of isotropy in the \mathbf{F} tensor, and also serves to preserve an axial field gradient quadric. For point defects in an isotropic homogeneous elastic continuum, the displacement, \mathbf{u} , at a position defined by the vector \mathbf{r} with respect to the point defect, is given by

$$\mathbf{u} = (\mathbf{r}/r^3)(\Delta V/4\pi\gamma_E), \quad (15)$$

²² E. F. Taylor and N. Bloembergen, *Phys. Rev.* **113**, 431 (1959).

²³ The parameter λ was originally defined by Bloembergen³ although less precisely. His parameter is identical to the present λ for the special case of uniaxial strain, but not for more general types of strain. λ is also often referred to as an "antiscreeing parameter," but usually with the warning that it is not the usual Sternheimer antiscreeing parameter.¹²

²⁴ J. D. Eshelby, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1956), Vol. 3, p. 79.

where ΔV is the change in volume per impurity. In a face-centered cubic lattice having atomic volume $a^3/4$, ΔV is related to the fractional change in lattice parameter per unit concentration of impurity, $a^{-1}(da/dc)$, by $\Delta V = (3a^3/4)a^{-1}(da/dc)$. $\gamma_E = 3(1-\sigma)/(1+\sigma)$ is about 1.5 for most metals. For copper we have used as Poisson's ratio σ the value 0.35, leading to $\gamma_E = 1.44$.

At a nucleus with coordinates $\mathbf{r} = (0,0,z)$ with respect to the impurity, the strain tensor will be given by

$$\epsilon_{xx} = \epsilon_{yy} = r^{-3}\Delta V/4\pi\gamma_E; \quad \epsilon_{zz} = -2r^{-3}\Delta V/4\pi\gamma_E; \\ \epsilon_{xy} = \epsilon_{yz} = \epsilon_{zx} = 0.$$

Therefore from Eqs. (13) and (14), in the face-centered cubic lattice, we have for the contribution to q associated with size effect,

$$q_\lambda = (1/e)(V_{zz} - \frac{1}{3}\nabla^2 V) = -(27/2^{\frac{3}{2}}\pi\gamma_E)a^{-1}(da/dc)\lambda r^{-3}. \quad (16)$$

It can be verified that the field gradient has axial symmetry about \mathbf{r} for any \mathbf{r} , with q_λ given by Eq. (16).

Combination of Valence and Size Effects

The two axially symmetric contributions q_α and q_λ can be combined algebraically, giving

$$q = q_\alpha + q_\lambda, \quad (17)$$

where q_α and q_λ are given by Eqs. (10) and (16). The two parameters α and λ are to be determined by fitting the experimental data. For any given choice of α and λ , the value of q can be computed for each of the neighbor shells surrounding the impurity, for each of the 14 elements for which Rowland presented experimental results. The wipeout fractions w_s for the individual shells are determined by the q values and by summation a predicted wipeout number $W = \sum n_s w_s$ for each of the 14 elements is computed. These predicted numbers are compared with Rowland's experimental values.² The latter are deduced from the slope at finite concentrations of the curve of the logarithm of intensity vs the logarithm of $(1-c)$, whereas our calculated numbers are actually the slope of this curve at the zero-concentration limit. The experimental data are in general well represented by straight lines passing through the point for pure copper at zero concentration. We assume that the actual slope at zero concentration is equal to the average slope between zero and the first point at finite concentration.

By a trial and error procedure we optimize α and λ with respect to the criterion of rms deviation between predicted and experimental wipeout numbers. It turns out, as might be expected, that the magnitude of α is determined by the data from elements with large valence difference Z' and small strain parameter $a^{-1}(da/dc)$, while the magnitude of λ is predominantly affected by the elements with the largest strain parameters. However, the separation is not complete, and for many elements both strain and charge contributions are

TABLE I. Comparison of experimental "wipeout numbers" with corresponding theoretical numbers including valence effect with and without size effect, for various solutes in copper.

1	2	3	4	5	6	7
Solute	Z'	$a^{-1}da/dc$	Experimental ^a	Valence effect only $\alpha=26$ $\lambda=0$	Wipeout numbers	
					Valence + size effect Algebraic ^b $\alpha=23$ $\lambda=-15$	Magnitudes ^c $\alpha=21$ $ \lambda =6.7$
Ag	0	0.17	25	14	31	20
Au	0	0.15	44	24	36	29
Mg	1	0.16	23	24	38	32
Zn	1	0.058	18	24	26	24
Cd	1	0.22	32	24	42	37
Al	2	0.067	27	31	38	30
Ga	2	0.078	38	34	41	33
In	2	0.26	48	29	47	44
Si	3	0.019	61	72	66	61
Ge	3	0.092	63	71	65	64
Sn	3	0.28	67	63	61	69
P	4	0.024	75	87	77	73
As	4	0.12	80	87	77	82
Sb	4	0.30	87	76	80	86
Rms from exp. ^d			3.3	10.5	7.3	5.6

^a Experimental wipeout numbers from Rowland, reference 2.^b q_α and q_λ added [Eq. (17)].^c $|q_\alpha|$ and $|q_\lambda|$ added [Eq. (18)].^d Column 4 is rms average of Rowland's quoted errors. Columns 5-7 give rms average of differences between experimental and theoretical wipeout numbers.

quite significant for many of the neighbor shells. For these cases the relative sign of α and λ is important. One expects and observes the following behavior. Let us assume that α is held fixed near its optimum value. Consider the value of the rms deviation from experiment as λ is varied from its optimum value towards zero. By definition, the rms deviation must increase at first. As the magnitude of λ is decreased, the assumed contribution due to strain will decrease and larger deviations from experiment arise for elements with larger strain and smaller Z' . Even for $\lambda=0$ there is significant correlation with experiment, as Rowland and KV have pointed out. If one continues to vary λ away from its optimum, the rms deviation begins to decrease again and has a very broad secondary minimum in the neighborhood of the negative of the optimum value of λ . This happens because the fit for elements with large Z' and small $a^{-1}(da/dc)$ is not disturbed, while there is improvement over a charge-only theory for these elements with large strain (in this case a significant contribution to wipeout number comes from outer shells where the strain effect is dominant). The elements for which both contributions are comparable do not fit as well as those for which λ/α has the optimum sign. However, the observed differences are smaller than one might have thought because the relative signs of q_α and q_λ are in general different in different shells, and there will be some cancellation. In order to see how important this cancellation is, we eliminated it by following out the consequences of the assumption

$$q = |q_\alpha| + |q_\lambda|. \quad (18)$$

The result of this trial showed that the difference between this and the simple algebraic addition of q_α and q_λ

is indeed quite great, and that moreover, with q given by Eq. (18), agreement with experiment is improved. Further discussion of this point is given below.

IV. RESULTS AND DISCUSSION

In column 1 of Table I are listed the impurities studied by Rowland² in copper, and in column 2, the valence difference Z' between copper and the impurity. Column 3 tabulates the strain parameter $a^{-1}da/dc$ obtained from Pearson's compilation²⁵ of lattice parameter data. In column 4 we give Rowland's experimental results. The rms deviation of 3.3 listed under column 4 is the rms average of the quoted experimental errors. In column 5 appear the values calculated for the wipeout number, W , assuming $\alpha=26$ and $\lambda=0$. For $\lambda=0$, this value of α , determined within about one unit, gave the lowest rms deviation. KV state their computed value, $\lambda=25.6$, is probably correct to within a factor of 2. We see, as already shown in a somewhat different way in references 2 and 7, that the charge-only theory accounts for the main features of the experimental data, particularly the dependence of W on the valence of the impurity. However, there are significant discrepancies. The value 10.5 for the rms deviation is very much greater than the value 3.3, characteristic of the experimental data. More striking, though, is the fact that the trend of W within each valence group except for $Z'=0$ is incorrectly predicted. The experimental results show that in every case but $Z'=0$, for a given Z' , W is larger for the impurity with the larger strain parameter. Thus antimony is larger than phosphorus, tin is larger than silicon, indium larger than aluminum, and so on. For

²⁵ W. B. Pearson, *Lattice Spacings and Structures of Metals and Alloys* (Pergamon Press, New York, 1958).

TABLE II. Theoretical contributions (in units of 10^{23} cm^{-3}) to the electric field gradient parameter q at different neighbor shells relative to the solute atom. q_α results from the valence effect and q_λ from the size effect. $q = q_\alpha + q_\lambda$; $\alpha = 23$; $\lambda = -15$.

	Shell No. of atoms in shell	1	2	3	4	5	6	7	8
		12	6	24	12	24	8	48	6
Ag	q_α	1.25	-0.52	0.28	0.04	-0.15	-0.03	0.08	0.05
	q_λ	3.31	1.17	0.64	0.41	0.30	0.22	0.18	0.15
Au	q_α	2.38	-1.02	0.56	0.07	-0.29	-0.04	0.16	0.09
	q_λ	2.92	1.03	0.56	0.37	0.26	0.20	0.16	0.13
Mg	q_α	2.17	-0.97	0.60	0.02	-0.29	-0.02	0.16	0.08
	q_λ	3.11	1.10	0.60	0.39	0.28	0.21	0.17	0.14
Zn	q_α	2.17	-0.97	0.60	0.02	-0.29	-0.02	0.16	0.08
	q_λ	1.13	0.40	0.22	0.14	0.10	0.08	0.06	0.05
Cd	q_α	2.17	-0.97	0.60	0.02	-0.29	-0.02	0.16	0.08
	q_λ	4.28	1.51	0.82	0.54	0.38	0.29	0.23	0.19
Al	q_α	4.22	-1.67	0.73	0.23	-0.41	-0.14	0.20	0.17
	q_λ	1.30	0.46	0.25	0.16	0.12	0.09	0.07	0.06
Ga	q_α	4.52	-1.78	0.77	0.26	-0.44	-0.15	0.21	0.18
	q_λ	1.52	0.54	0.29	0.19	0.14	0.10	0.08	0.07
In	q_α	3.87	-1.53	0.68	0.21	-0.39	-0.12	0.18	0.16
	q_λ	5.06	1.79	0.97	0.63	0.45	0.34	0.27	0.22
Si	q_α	4.09	-2.31	2.05	-0.34	-0.90	0.17	0.58	0.13
	q_λ	0.37	0.13	0.07	0.05	0.03	0.02	0.02	0.02
Ge	q_α	4.00	-2.27	2.01	-0.34	-0.88	0.17	0.57	0.12
	q_λ	1.79	0.63	0.34	0.22	0.16	0.12	0.10	0.08
Sn	q_α	3.46	-1.97	1.76	-0.30	-0.77	0.16	0.50	0.11
	q_λ	5.45	1.93	1.05	0.68	0.49	0.37	0.29	0.24
P	q_α	-1.68	-0.71	2.34	-1.21	-0.82	0.64	0.68	-0.15
	q_λ	0.47	0.16	0.09	0.06	0.04	0.03	0.02	0.02
As	q_α	-1.72	-0.71	2.36	-1.22	-0.83	0.65	0.68	-0.15
	q_λ	2.33	0.83	0.45	0.29	0.21	0.16	0.13	0.10
Sb	q_α	-1.02	-0.77	2.07	-1.01	-0.74	0.54	0.60	-0.11
	q_λ	5.84	2.06	1.12	0.73	0.51	0.40	0.32	0.26

these cases, the theory on the other hand either predicts the reverse behavior or no change. It should be noted that the fact that the theoretical W is the same for Mg, Zn, and Cd is due to the fact that in the approximation used by Kohn and Vosko, the phase shifts for these elements had to be chosen to be the same. In column 6 of Table I we give the theoretical wipeout numbers for $\alpha=23$, and $\lambda=-15$. In computing the resultant q , q_α and q_λ were added algebraically. These values of α and λ are the optimum values with respect to rms deviation of W . The addition of strain thus changes the optimum value of α only slightly. The value of α , in any case, can be considered in good agreement with the KV theoretical estimate.

The inclusion of q_λ produces a marked improvement in the agreement between theory and experiment. The rms deviation is reduced to 7.3. Of more physical significance than the rms deviation criterion is the fact that the discrepancy in ordering of elements within valence groups is markedly reduced.

In column 7 of Table I we give the optimum case of a calculation in which the magnitudes of q_α and q_λ were added, rather than taking the algebraic sum. The optimum enhancement factors in this case are $\alpha=21$ and $|\lambda|=6.7$. It is apparent that the agreement of column 7 with the experimental results is somewhat better than that of column 6. The rms deviation is reduced from 7.3 to 5.6 and, without exception, all elements are correctly ordered within each valence group.

This improvement, resulting from the arbitrary addition of magnitudes, may be physically significant rather than fortuitous. Thus in the algebraic model, the large degree of cancellation of size and valence effects may be exaggerated compared to that in a more correct model.

The existence of deviations from cylindrical symmetry in either the size or valence contributions would require the addition of the individual components of the field gradient tensor at each lattice site rather than the simple addition of q_α and q_λ . The amount of accidental cancellation from the addition of independent tensor components would presumably be quite a bit less than from the simple scalar addition of q_α and q_λ . Such deviations from cylindrical symmetry may occur even with a radial strain if, as has already been pointed out, the field gradient-strain tensor shows cubic as opposed to spherical symmetry. Furthermore, more realistic descriptions of the strain field about a point imperfection in a cubic crystalline solid give rather strong deviations from a purely radial strain field characteristic of an isotropic homogeneous solid.²⁶

Table II lists the values of q_α and q_λ out to the eighth shell for the case $\alpha=23$, $\lambda=-15$, $q=q_\alpha+q_\lambda$. It is seen that over-all the two effects are of the same order of magnitude. For example, for phosphorus, which is in

²⁶ For example, see J. B. Gibson, A. N. Goland, M. Milgram, and G. H. Vineyard, Phys. Rev. **120**, 1229 (1960) and also work cited in reference 20 of their paper. We are indebted to Dr. Vineyard for discussing the results obtained by machine computations relevant to the static lattice vacancy for a model representing copper, prior to publication in the above and a forthcoming paper.

TABLE III. Contributions $n_s w_s$ to wipeout number W arising from the different neighbor shells relative to solute. $q = q_\alpha + q_\lambda$; $\alpha = 23$; $\lambda = -15$.

Shell	1	2	3	4	5	6	7	8	$\Sigma n_s w_s = W$
n_s , No. of atoms in shell	12	6	24	12	24	8	48	6	
Ag	12	1.6	15.7	0.9	0.1	0.0	0.6	0.0	31
Au	12	0.0	22.4	0.7	0.0	0.0	1.2	0.0	36
Mg	12	0.0	23.5	0.6	0.0	0.0	1.3	0.0	38
Zn	12	1.1	12.0	0.0	0.1	0.0	0.4	0.0	26
Cd	12	0.9	24.9 ^b	2.0	0.0	0.1	2.2	0.1	42
Al	12	5.9	18.0	0.5	0.5	0.0	0.8	0.1	38
Ga	12	6.0	20.8	0.8	0.5	0.0	1.0	0.1	41
In	12	0.1	24.7 ^b	6.5	0.0	0.1	3.6	0.2	47
Si	12	6.0	24.0	0.2	13.9	0.0	9.8	0.0	66
Ge	12	6.2 ^b	24.0	0.0	8.6	0.2	13.7	0.0	65
Sn	12	0.0	24.0	0.5	0.4	1.1	22.8	0.2	61
P	12	0.9	24.0	11.5	10.6	2.4	16.2	0.0	77
As	(12) ^a	0.0	24.0	8.2	5.4	4.0	23.3	0.0	77
Sb	12	6.1 ^b	24.0	0.2	0.2	5.5	31.5	0.0	80

^a We have assumed $w_s = 1$ rather than the computed $w_s = 0.2$ since the latter results from the approximate cancellation of large contributions q_α and q_λ and, in the first neighbor shell, deviations from the idealized models for size and valence contributions are expected to be so large that this fortuitous cancellation will not occur.

^b The value of w_s can be slightly greater than unity where the contribution to the derivative curve at the original maximum is negative and small.

the highest Z' group but has a small strain parameter, q_α is considerably greater than q_λ . For antimony, with the same Z' but a large strain parameter, q is smaller for the first, second, and eighth shells and larger for the rest. Conversely, for gold where $Z' = 0$ and valence effects might be expected to be small, they are actually of the same order of magnitude as the size effects. It should be borne in mind in scanning this table that for $w(k) \geq 5\%$, that is for the intensity of a shell to be reduced by 5% or more, q must be $\geq 0.4 \times 10^{23} \text{ cm}^{-3}$.

In Table III we give $n_s w_s$ out to the eighth shell for the impurities listed by Rowland. Contributions to W were negligible in all cases in the eighth shell due to the small q 's and the small number (6) of atoms in this shell. If the "all or nothing" model were a good approximation, the entries in this table would either be zero or equal to the number of atoms in the shell concerned.

It is of interest to compare the value of $|\lambda|$ deduced in the present investigation with other values appearing in the literature. Averbuch⁹ *et al.* and Faulkner^{10,11} have studied the NMR line of cold-worked pure copper and find an increase in the second moment and in the linewidth. By correlating the NMR data with independent measurements of the strain they are able to estimate $|\lambda|$, under the assumption that the gradients are due entirely to strain effects. Averbuch *et al.* obtained $|\lambda| \sim 1$, and Faulkner obtained a lower limit²⁷ for $|\lambda|$ of about 0.4. These values are an order of magnitude smaller than that deduced from our model, even if we

were to accept the value $|\lambda| = 6.7$ obtained by adding the magnitudes of q_α and q_λ .

In discussing this disagreement it should first be pointed out that it is not really obvious in the experiments on pure copper that the electric field gradients involved are really due to strain effects alone, as assumed by Averbuch *et al.* and Faulkner. The broadening in cold-worked, pure copper is presumed to be the first-order effects of neutral imperfections such as dislocations. However, the fact that an imperfection is neutral is not in itself a valid reason for assuming the charge effect to be small compared to the strain effect. For example, we have found, as shown in Table II, that for the neutral impurity, silver, q_α is about $\frac{1}{3}$ of q_λ for the close neighbors, and for the neutral impurity, gold, they are about equal. To estimate the magnitude of the charge effect for a dislocation, it would be necessary to make a calculation comparable to the KV calculation. If such a theoretical calculation showed that to account for the small broadening would require (even assuming a value of λ considerably smaller than that deduced by Averbuch *et al.* and Faulkner) an α considerably less than 20, then a further contradiction between these experiments and the impurity experiments would be revealed. That is, the experiments on cold-worked, pure copper would indicate values of both α and λ considerably smaller than the values deduced from the data on impurities.

One possible key as to whether this discrepancy should be regarded as a serious criticism of our model lies in Rowland's linewidth data. Rowland has shown that for the impurities, Zn, Ge, and As, the charge-only theory predicts a broadening while the experimental line actually narrows in the alloys. For Ga as impurity the experimental line broadens but much less than the theory predicts. Rowland ascribes the disagreement to the model used for the theoretical calculation. We have

²⁷ E. A. Faulkner¹¹ points out that his value of λ may be regarded as a lower limit because of the following assumptions: (1) Since strain is deduced from stored energy, it is implicit that all the stored energy is associated with elastic strain; (2) all regions of the cold-worked specimen are assumed to contribute equally to the NMR signal. The latter assumption is also involved in the work of Averbuch *et al.*⁹ It is difficult to estimate the error involved here, but we feel that a factor of two is not unlikely, but would not expect much more.

also investigated the broadening for Ge with our model and get qualitative agreement with Rowland's theory. It seems very unlikely to us that any calculation involving quadrupole interactions will lead to a line narrowing. It seems much more likely that the discrepancy is real and is due to a narrowing mechanism which has not been included in the theory and which is of the same order of magnitude as the quadrupole effect. Until the line narrowing is understood one should be cautious in deducing the values of either α or λ from measurements based on linewidths or second moments.

V. CONCLUSIONS

It has been demonstrated that the introduction of strain-induced electric-field gradients described by a single parameter characteristic of the solvent materially improves agreement between experimental and theoretical wipeout numbers in dilute copper alloys. The magnitude of the strain-induced field gradients deduced from the present model are comparable in magnitude with the corresponding field gradients associated with the impurity charge. This conclusion does not contradict the findings of Rowland and Kohn and Vosko that the

field gradient associated directly with the screened impurity charge by itself accounts for the main features of nuclear quadrupole effects in these alloys.

The parameter λ describing the magnitude of the field gradient associated with a given strain field that is obtained from the present results is appreciably larger than that found in experiments based upon measurements of NMR line broadening in cold-worked pure copper. It is believed that this apparent discrepancy is in part correlated with discrepancies between theoretical and observed line broadening in the alloys.

There is some indication from the present results that still further improvement in the agreement between experimental and theoretical wipeout numbers can be brought about by a more detailed treatment of effects leading to lower than axial symmetry in the field gradients.

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