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

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Theory of Nuclear Resonance Intensity in Dilute Alloys*†

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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 Rowland[1] and Rowland[2] 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

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

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

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

field gradients are about two orders of magnitude too small at the more distant lattice sites.

Recently Friedel[3] has pointed out that on the basis of a self consistent treatment of an electron gas in the vicinity of a solute atom one expects the screening charge to fall off much more slowly with distance, namely as r^{-3} multiplied by a sinusoidal function of r. A similar behavior was also obtained by Langer and Vosko[4] using an approximate many electron perturbation theory.[5] A survey of the experimental data at once suggests that this long range screening might well be responsible for the field gradients. For they are roughly consistent with the assumption that the field gradients behave as Z'/r^3 where Z' is the valence difference between the impurity and copper.

In this paper we make a rough quantitative estimate of the field gradients associated with such an oscillating screening charge. In Sec. 2 we derive an expression for the field gradients in terms of the screening phase shifts of electrons at the Fermi surface due to solutes, and an enhancement factor α due to the Bloch character of the electrons as well as to antishielding effects of the core. The phase shifts are calculated in Sec. 3 from the Friedel sum rule[3] and the measured values of residual resistivities. The enhancement factor α is calculated in Sec. 4 with the help of a simple orthogonalized plane wave procedure. In Sec. 5 we shall show that our results account for all the general features of Rowland's experiments and give quantitative agreement to better than a factor of two. In Sec. 6 we use this agreement to draw conclusions about the sharpness of the Fermi surface in copper.

2. GENERAL THEORY

In this section we shall derive an expression for the oscillating part of the screening charge around a solute atom in a metal. We follow closely the procedure of Friedel,[3] except that we describe the electrons by Bloch waves rather than by plane waves.

A solute atom in a metal will be considered to give rise to a perturbing potential $U'(r)$ acting on the Bloch electrons. This potential may be thought of as obtained from a self-consistent calculation and includes the effect of screening. However, we shall see that for our purposes it need not actually be computed. The electrons are then described by the following Schrödinger equation

$$[-(\hbar^2/2m)\nabla^2+U(\mathbf{r})+U'(\mathbf{r})]\psi=E\psi, \tag{2.1}$$

where $U(\mathbf{r})$ is the periodic potential in the absence of the solute.

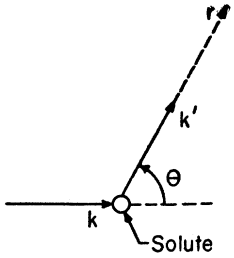

FIG. 1. Scattering of a Bloch wave by a solute atom.

When U' vanishes, the solutions of (2.1) are the Bloch waves $\varphi_{\mathbf{k}}(r)$, belonging to the conduction band in question, which we normalize as follows:

$$\frac{1}{(2\pi)^3}\int \varphi_{\mathbf{k}}^*(\mathbf{r})\varphi_{\mathbf{k}'}(\mathbf{r})d\mathbf{r}=\delta(\mathbf{k}-\mathbf{k}'). \tag{2.2}$$

For simplicity we shall assume that the conduction band $E_{\mathbf{k}}$ is spherically symmetrical.

We are now interested in the asymptotic form of the solutions $\psi_{\mathbf{k}}$ of (2.1), corresponding to an incident Bloch wave $\varphi_{\mathbf{k}}$ and an outgoing scattered wave. We shall take the solute atom to be situated at the origin. In complete analogy with the theory of plane wave scattering, one finds

$$\psi_{\mathbf{k}}(\mathbf{r})=\varphi_{\mathbf{k}}(\mathbf{r})+[f(\mathbf{k},\mathbf{k}')/r]\varphi_{\mathbf{k}'}(\mathbf{r}), \tag{2.3}$$

where $|\mathbf{k}'|=|\mathbf{k}|$, and furthermore

$$\mathbf{k}'=k'(\mathbf{r}/r), \tag{2.4}$$

that is $\mathbf{k}'$ is in the same direction as $\mathbf{r}$. (See Fig. 1.) This property can be seen as follows. An electron arriving at $\mathbf{r}$ after being scattered at the origin has a velocity vector $\mathbf{v}$ in the direction of $\mathbf{r}$. Because of the assumed spherical symmetry of $E_{\mathbf{k}}$, its $\mathbf{k}$ vector is parallel to $\mathbf{v}$ and hence also to $\mathbf{r}$.

In the absence of more detailed information we assume that $f(\mathbf{k},\mathbf{k}')$ depends only on the magnitude of $\mathbf{k}$ and the angle θ between $\mathbf{k}$ and $\mathbf{k}'$ or $\mathbf{k}$ and $\mathbf{r}$ (Fig. 1), and shall write it as $f_k(\theta)$. We can then expand $f_k(\theta)$ in spherical harmonics in the usual way,

$$f_k(\theta)=\frac{1}{2ik}\sum_{l=0}^{\infty}(2l+1)(e^{2i\eta_l(k)}-1)P_l(\cos\theta), \tag{2.5}$$

where the η_l's are phase shifts. For large r, the excess electron density contributed by the wave function $\psi_{\mathbf{k}}$ can be written as

$$\begin{aligned}\delta n_{\mathbf{k}}(\mathbf{r})&\equiv|\psi_{\mathbf{k}}(\mathbf{r})|^2-|\varphi_{\mathbf{k}}(r)|^2\\&=\delta n_{\mathbf{k}}^{(1)}+\delta n_{\mathbf{k}}^{(2)},\end{aligned} \tag{2.6}$$

where

$$\delta n_{\mathbf{k}}^{(1)}(\mathbf{r})=(1/r)[\varphi_{\mathbf{k}}^*(\mathbf{r})f_k(\theta)\varphi_{\mathbf{k}'}(\mathbf{r})+\text{c.c.}], \tag{2.7}$$

and

$$\delta n_{\mathbf{k}}^{(2)}(\mathbf{r})=(1/r^2)|f_k(\theta)|^2|\varphi_{\mathbf{k}'}(\mathbf{r})|^2. \tag{2.8}$$

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[3] J. Friedel, Phil. Mag. 43, 153 (1952); *Advances in Physics* edited by N. F. Mott (Taylor and Francis, Ltd., London, 1954), Vol. 3, p. 446; Suppl. Nuovo cimento 2, 287 (1958).

[4] J. S. Langer and S. H. Vosko, J. Phys. Chem. Solids 12, 196 (1959).

[5] Some confirmation of a similar effect has already been presented by A. Blandin and E. Daniel [J. Phys. Chem. Solids **10**, 126 (1959)] who have studied the shift and broadening of the Knight shift primarily in alloys of Ag which has no quadrupole moment. However, here there is no conclusive evidence that the effects extend beyond the third nearest neighbor.

The total excess density at **r** is

$$\delta n(\mathbf{r})=\frac{2}{(2\pi)^3}\int_{k<k^0}\delta n_{\mathbf{k}}(\mathbf{r})d\mathbf{k},\tag{2.9}$$

where k^0 is the wave number at the Fermi surface.

To evaluate $\delta n_{\mathbf{k}}^{(1)}$ we first introduce the periodic parts of the Bloch waves

$$\varphi_{\mathbf{k}}(\mathbf{r})=u_{\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}},\tag{2.10}$$

which gives

$$\delta n^{(1)}(\mathbf{r})=\frac{2}{(2\pi)^3}\frac{1}{r}\bigg[\int_{k<k^0}u_{\mathbf{k}}{}^*(\mathbf{r})u_{\mathbf{k}'}(\mathbf{r})\times f_k(\theta)e^{-ikr(\cos\theta-1)}d\mathbf{k}+\text{c.c.}\bigg].\tag{2.11}$$

For large r only the exponential in (2.11) is a rapidly varying function of the angle θ between **k** and **r**. This allows us to extract the dominant term by integrating (2.11) by parts with respect to θ. For, let $F(\theta)$ be a slowly varying function of θ. Then

$$\int_0^\pi F(\theta)e^{-ikr(\cos\theta-1)}d(\cos\theta)=\frac{1}{ikr}F(\pi)e^{2ikr}-\frac{1}{ikr}F(0)+0\left(\frac{1}{r^2}\right).\tag{2.12}$$

Applying this result to (2.11) gives

$$\delta n^{(1)}(\mathbf{r})=\frac{1}{2\pi^2}\frac{1}{r^2}\bigg\{\bigg[\int_0^{k^0}e^{2ikr}\frac{f_k(\pi)}{i}u_{-\mathbf{k}}{}^*(\mathbf{r})u_{\mathbf{k}}(\mathbf{r})kdk+\text{c.c.}\bigg]-\bigg[\int_0^{k^0}\frac{f_k(0)}{i}u_{\mathbf{k}}{}^*(r)u_{\mathbf{k}}(\mathbf{r})kdk+\text{c.c.}\bigg]\bigg\}.\tag{2.13}$$

The integrals are over the magnitude of **k** only, its direction being fixed in the direction of **k′** or **r**. The second bracket in (2.13) is precisely cancelled by the contribution of $\delta n_k^{(2)}(\mathbf{r})$, in virtue of the well-known optical theorem

$$\int d\Omega|f_k(\theta)|^2=(4\pi/ik)\,\text{Im}f_k(0).\tag{2.14}$$

Further we may use the identity

$$u_{-\mathbf{k}}{}^*(\mathbf{r})=u_{\mathbf{k}}(\mathbf{r})\tag{2.17}$$

to obtain

$$\delta n(\mathbf{r})=\frac{1}{2\pi^2}\frac{1}{r^2}\bigg(\int_0^{k^0}e^{2ikr}\frac{f_k(\pi)}{i}[u_{\mathbf{k}}(\mathbf{r})]^2kdk+\text{c.c.}\bigg).\tag{2.16}$$

Again, for large r, only the exponential is a rapidly varying function of k so that one may integrate by parts as in Eq. (2.12). This gives the final result that

$$\delta n(\mathbf{r})=-(1/4\pi^2)(1/r^3)\{\exp(2ik^0r)[u_{\mathbf{k}^0}(\mathbf{r})]^2\times k^0f_{k^0}(\pi)+\text{c.c.}\},\tag{2.17}$$

where $\mathbf{k}^0$ points in the direction of **r**.[6] In the special case of plane waves $[u_{k^0}(\mathbf{r})\equiv1]$, Eq. (2.17) reduces with the help of (2.5), to Friedel's result

$$\delta n_{\text{free}}(r)\equiv\frac{1}{2\pi^2r^3}\sum_l(2l+1)\times[-\sin\eta_l\cos(2k^0r+\eta_l-l\pi)],\tag{2.18}$$

which may be expressed as

$$\delta n_{\text{free}}(r)=A\cos(2k^0r+\varphi)/r^3,\tag{2.19}$$

where

$$A=\frac{1}{2\pi^2}\Big(\{\sum_l(2l+1)[-\sin\eta_l\cos(\eta_l-l\pi)]\}^2+\{\sum_l(2l+1)[-\sin\eta_l\sin(\eta_l-l\pi)]\}^2\Big)^{\frac{1}{2}},\tag{2.20}$$

and

$$\varphi=\tan^{-1}\frac{\sum_l(2l+1)\sin\eta_l\cos(\eta_l-l\pi)}{\sum_l(2l+1)\sin\eta_l\sin(\eta_l-l\pi)}.\tag{2.21}$$

Here the η_l's are the scattering phase shifts at the Fermi surface.

The oscillating electron density (2.17) gives rise to electric field gradients which act on the quadrupole moments of the Cu nuclei. To compute the interaction between the conduction electrons and the Cu nucleus situated at a distant lattice point r_n it is convenient to take the z zxis along $\mathbf{r}_n$ and to define the relative coordinate (see Fig. 2)

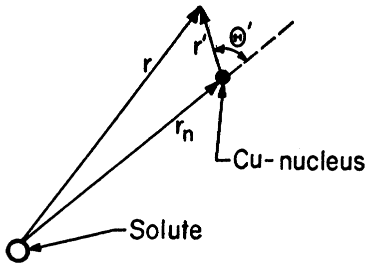

FIG. 2. Coordinate transformation.

$$\mathbf{r}'\equiv\mathbf{r}-\mathbf{r}_n.\tag{2.22}$$

The electrostatic potential due to (2.17) is given by

$$V(\mathbf{r}')=-e\int\frac{\delta n(\mathbf{r}_n+\mathbf{r}'')}{|\mathbf{r}''-\mathbf{r}'|}d\mathbf{r}'',\tag{2.23}$$

and may be expanded in spherical harmonics. To a good approximation we may take $V(\mathbf{r}')$ as axially

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[6] It may be noted that $u_{k^0}(\mathbf{r})$ occurs in (2.17) just squared, not absolute value squared.

symmetric and write near $\mathbf{r}'=0$,

$$V(\mathbf{r}')=V_0+z'(\partial V/\partial z')+\cdots. \tag{2.24}$$

For our purposes the relevant term is associated with the spherical harmonic P_2 and is given by

$$V_2(\mathbf{r}')=\tfrac{1}{2}eq'r'^2P_2(\cos\Theta'), \tag{2.25}$$

where the constant q' is given by

$$q'=-\int\frac{\delta n(\mathbf{r}_n+\mathbf{r}')}{r'^3}(3\cos^2\Theta'-1)d\mathbf{r}'. \tag{2.26}$$

However the actual field gradient at a nucleus is not yet given by q' but must be corrected for effects of core polarization.[7–9] This leads to a modified constant q, given by

$$q=-\int\frac{\delta n(\mathbf{r}_n+\mathbf{r}')}{r'^3}[1+\gamma(r')](3\cos^2\Theta'-1)d\mathbf{r}', \tag{2.27}$$

where $\gamma(r')$ is the so-called antishielding factor.[9] This is the quantity which we must calculate at various lattice sites and compare with experiment.

It is useful to write out (2.27) in a way which exhibits explicitly its dependence on the phase-shifts and on a $\langle 1/r^3\rangle$-type integral involving the Bloch functions and the antishielding factor $\gamma(r')$. The main contribution to the integral in (2.27) comes from small values of r' because of the $1/r'^3$ factor. Since our theory assumes that r is large we may replace the factor r^{-3} in (2.17) by r_n^{-3}. For the same reason $\mathbf{k}^0$ may be taken in the direction of $\mathbf{r}_n$. With these simplifications and expressing $f_{k^0}(\theta)$ in terms of the phase shifts (2.17) becomes

$$\delta n(\mathbf{r}_n+\mathbf{r}')=\frac{1}{4\pi^2}\frac{1}{r_n^3}\sum_l(2l+1)(-1)^{l+1}\sin\eta_l \times\exp[i(2k^0r_n+\eta_l)][\varphi_{\mathbf{k}^0}(\mathbf{r}')]^2+\text{c.c.} \tag{2.28}$$

Substituting this expression in (2.27) we obtain at the nth lattice site

$$q=\alpha\frac{8\pi}{3}\frac{A\cos(2k^0r_n+\varphi)}{r_n^3}, \tag{2.29}$$

where

$$\alpha=\frac{\int[\varphi_{\mathbf{k}^0}(\mathbf{r}')]^2P_2(\cos\Theta')\{[1+\gamma(r')]/r'^3\}d\mathbf{r}'}{\int\exp(2i\mathbf{k}^0\cdot\mathbf{r}')P_2(\cos\Theta')(1/r'^3)d\mathbf{r}'}. \tag{2.30}$$

This α is an enhancement factor, which measures the increase of q over its value in a plane wave theory without antishielding. Its magnitude will turn out to be about 25 for copper. A and φ are determined by the phase shifts η_l, according to Eqs. (2.20) and (2.21).

3. DETERMINATION OF PHASE SHIFTS

We see from Eq. (2.28) that the oscillating part of the electron charge density is determined entirely by the scattering phase shifts η_l for electrons at the Fermi surface, and by the form of the Bloch waves. In this section we shall estimate the values of η_l for various substitutional impurities in Cu.

One method is especially simple because it does not require explicit knowledge of the effective scattering potential $U'(\mathbf{r})$. We recall first the Friedel[3] sum rule

$$Z'=\frac{2}{\pi}\sum_0^\infty(2l+1)\eta_l(k^0), \tag{3.1}$$

where Z' is the valence difference between the solute atom and copper. This equation results from the requirement that any excess charge on the impurity ion be exactly compensated by a shielding charge of the conduction electrons.

Secondly, the residual resistance of a dilute alloy of copper is given by

$$\Delta\rho=(\hbar k^0c/e^2)\sigma_e, \tag{3.2}$$

where c is the atomic concentration of the solute and σ_e is the effective scattering cross section at the Fermi surface given by

$$\sigma_e=\int(1-\cos\theta)|f_{k^0}(\theta)|^2d\Omega =\frac{4\pi}{k^{0 2}}\sum_{l=1}^\infty l\sin^2(\eta_{l-1}-\eta_l). \tag{3.3}$$

If we now make the assumption that only η_0 and η_1 are appreciable,[10] we can attempt to use the known values of Z' and σ_e to determine these phase shifts from (3.1) and (3.3). This procedure gives the results listed in Table I for solutes in Groups I, III, IV, and V. For solutes in Group II, the measured resistance is smaller than any value obtainable with η_0 and η_1 only, which satisfy the sum rule (3.1). For these materials η_0 and η_1 were chosen to give the lowest possible resistance compatible with (3.1). These values are also listed in Table I. The last two columns of Table I, give the total amplitude and phase of the oscillatory part of the electron density, defined in Eq. (2.28). It will be noticed that the values of A and φ are strongly correlated with with Z'. This is due to the fact that the observed residual resistivity is very similar for solutes of equal Z'. (See Table I.)

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[7] H. M. Foley, R. M. Sternheimer, and D. Tycko, Phys. Rev. **93**, 734 (1954).

[8] R. H. Sternheimer and H. M. Foley, Phys. Rev. **102**, 731 (1956).

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

[10] If one represents U' by a screened Coulomb potential, one does indeed find values of η_2 so small as not to affect our further conclusions by more than about 25%.

TABLE I. Scattering characteristics of different impurities in copper.

Impurity	Residual resistivity[a] $\Delta\rho$	η_0	η_1	A	φ
Group I ($Z'=0$)					
Ag	0.14	0.136	−0.045	0.0138	0.0454[b]
Au	0.55	0.275	−0.092	0.0272	0.0906[b]
Group II ($Z'=1$)					
Mg	0.65	0.521	0.350	0.0276	0.194
Zn	0.32	0.521	0.350	0.0276	0.194
Cd	0.30	0.521	0.350	0.0276	0.194
Group III ($Z'=2$)					
Al	1.25	2.715	0.142	0.0408	−0.138
Ga	1.42	2.684	0.153	0.0434	−0.147
In	1.06	2.752	0.130	0.0376	−0.127
Group IV ($Z'=3$)					
Si	3.95	2.983	0.576	0.0889	0.516
Ge	3.79	3.005	0.569	0.0873	0.518
Sn	2.88	3.135	0.526	0.0765	0.523
Group V ($Z'=4$)					
P	6.7	3.396	0.962	0.1153	1.034
As	6.8	3.382	0.967	0.1164	1.036
Sb	5.4	3.581	0.901	0.1003	0.996

[a] Units —μohm —cm per atomic percent solute.

[b] Actually only the relative signs of η_0 and η_1 can be determined from the residual resistance. Reversing the sign leaves A unchanged but the sign of φ changes; this does not affect the conclusions that follow.

The quantities A and φ can also be calculated "from first principles." For this purpose we treat the electrons as a free electron gas (with uniform positive background) in the presence of an immersed charge $Z'e$. Using many-body perturbation theory one can calculate, approximately, the change of the electron density due to the immersed charge to first order in $Z'e$. This was done by Langer and Vosko[4] who find for copper

$$\delta n(\mathbf{r})=0.0236Z'\frac{\cos(2k^0r+\pi)}{r^3}. \qquad (3.4)$$

In Table II this result is compared with the mean values obtained from the semiempirical procedure described above.

We see that the two methods give quite similar results for the amplitudes A. Of the two sets of values we prefer that obtained by the semiempirical method, since effects of the Bloch wave nature of the electron wave functions and of terms omitted in the approximate perturbation theoretic treatment are contained in the "empirical" values of η_0 and η_1.

TABLE II. Amplitude and phase of oscillatory electron density.

	A		φ	
Z'	Perturbation theory	Semiempirical method	Perturbation theory	Semiempirical method
0	0.0000	0.0205	π	0.0680
1	0.0236	0.0276	π	0.194
2	0.0472	0.0406	π	−0.137
3	0.0708	0.0842	π	0.519
4	0.0944	0.1107	π	1.022

4. ESTIMATE OF α

Before we can evaluate the field gradients at the positions of Cu-nuclei in the vicinity of a solute atom, we must still estimate the quantity

$$\alpha=\frac{\int[\varphi_{\mathbf{k}}(\mathbf{r}')]^2P_2(\cos\Theta')\{[1+\gamma(r')]/(r')^3\}d\mathbf{r}'}{\int[e^{2i\mathbf{k}\cdot(\mathbf{r}')}]P_2(\cos\Theta')(1/r'^3)d\mathbf{r}'}, \qquad (4.1)$$

where $\mathbf{k}$ is the wave vector on the Fermi surface in the direction of $\mathbf{r}_n$ and $\mathbf{r}_n$ is the position of the Cu nucleus in question relative to the solute atom, $\mathbf{r}'$ the position vector relative to $\mathbf{r}_n$, Θ' is the angle between $\mathbf{k}$ and $\mathbf{r}'$ and $\gamma(\mathbf{r}')$ is the antishielding factor (see Fig. 2). We have made only a rough determination of α which we shall now describe.

The denominator in (4.1) has the value $-4\pi/3$. To estimate the numerator we need an approximate form of the Bloch wave $\varphi_{\mathbf{k}}(\mathbf{r}')$. We anticipate (and later verify) that the main contribution to the integral comes from regions in $\mathbf{r}'$ space which lie well inside the atomic cell. In this cell we approximate $\varphi_{\mathbf{k}}$ by a single orthogonalized plane wave

$$\varphi_{\mathbf{k}}(\mathbf{r}')=(1/N^{\frac{1}{2}})[e^{ik\cdot z'}-\sum_{n,l}B_{nl}\psi_{n,l,0}(\mathbf{r}')]. \qquad (4.2)$$

Here the $\psi_{n,l,0}$ are the real normalized atomic core functions; the $B_{n,l}$ are coefficients chosen to make φ_k orthogonal to the $\psi_{n,l,0}$ and are given by

$$B_{n,l}=\int e^{+ikz'}\psi_{n,l,0}(\mathbf{r}')d\mathbf{r}'; \qquad (4.3)$$

the normalization constant is so chosen as to make

$$\frac{1}{\Omega}\int_{\Omega}|\varphi_{\mathbf{k}}(r')|^2d\mathbf{r}'=1, \qquad (4.4)$$

where Ω is the volume of the atomic cell:

$$N=1-(1/\Omega)\sum_{n,l}|B_{n,l}|^2. \qquad (4.5)$$

The atomic core functions were taken from a Hartree-Fock calculation of Cu^+.[11] The $B_{n,l}$ have the following values in atomic units:

$$\begin{aligned}&B_{1,0}=0.0952,\\&B_{2,0}=-0.663,\quad B_{2,1}=(0.092)i,\\&B_{3,0}=2.919,\quad B_{3,1}=(-1.639)i,\quad B_{3,2}=-0.920.\end{aligned} \qquad (4.6)$$

The function $[\varphi_{\mathbf{k}}(\mathbf{r}')]^2$, occurring in (4.1) was then decomposed into spherical harmonics giving

$$[\varphi_{\mathbf{k}}(\mathbf{r}')]^2=\cdots+G(r')P_2(\cos\Theta')+\cdots. \qquad (4.7)$$

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[11] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A157**, 490 (1936).

TABLE III. Values of q in units 10^{23} cm^{-3} at different lattice sites relative to solute atom.

Shell	1	2	3	4	5	6	7	8
Number of atoms in shell	12	6	24	12	24	8	48	6
Group I ($Z'=0$)								
Ag	1.36	-0.57	0.30	0.047	-0.16	-0.028	0.086	0.054
Au	2.59	-1.11	0.61	0.072	-0.32	-0.045	0.17	0.10
Group II ($Z'=1$)								
Mg	2.36	-1.06	0.65	0.027	-0.32	-0.020	0.18	0.089
Zn	2.36	-1.06	0.65	0.027	-0.32	-0.020	0.18	0.089
Cd	2.36	-1.06	0.65	0.027	-0.32	-0.020	0.18	0.089
Group III ($Z'=2$)								
Al	4.60	-1.82	0.79	0.25	-0.45	-0.15	0.22	0.19
Ga	4.92	-1.94	0.84	0.28	-0.48	-0.16	0.23	0.20
In	4.22	-1.67	0.74	0.23	-0.42	-0.13	0.20	0.17
Group IV ($Z'=3$)								
Si	4.46	-2.52	2.23	-0.37	-0.98	0.19	0.63	0.14
Ge	4.36	-2.47	2.19	-0.37	-0.96	0.18	0.62	0.13
Sn	3.77	-2.15	1.92	-0.33	-0.84	0.17	0.55	0.12
Group V ($Z'=4$)								
P	-1.83	-0.77	2.55	-1.32	-0.89	0.70	0.74	-0.16
As	-1.87	-0.77	2.57	-1.33	-0.90	0.71	0.74	-0.16
Sb	-1.11	-0.84	2.26	-1.10	-0.81	0.59	0.65	-0.12

The function $\gamma(r')$ was obtained from a paper by Foley, Sternheimer, and Tycko,[7] and an adjustment was made to allow for their later correction to $\gamma(\infty)$.[8] The integral (4.1) was then evaluated numerically first over an equivalent atomic sphere. It was found that the major portion comes from distances less than a_0, where γ is approximately zero.[12] The integral over the atomic sphere contributes the value 23.3 to α. The contribution from the outside region was roughly estimated at 2.3. Thus our final value is

$$\alpha=25.6. \tag{4.8}$$

This is probably accurate to better than a factor of 2.

5. RESULTS AND COMPARISON WITH EXPERIMENT

We are now in a position to list the values of q at various lattice sites relative to a given solute atom, by using Eq. (2.29), the values of A and φ listed in Table I and the value $\alpha=25.6$. (See Table III.)

The nuclear resonance frequency of a Cu-nucleus near a solute atom is shifted by the field gradient due to the solute. The magnitude of this shift depends on the value of q as well as the orientation of the magnetic field. Since the field has a random orientation with respect to the crystal axes of the particles in the specimen, the contribution to the resonance line from shells of Cu nuclei in which q is large will be correspondingly broad. If this breadth becomes too large, the nuclei of such shells make no contribution to the observed line.

Rowland[2] has used our values of q for successive shells near a Ge solute, with a numerical factor as an adjustable parameter, to calculate the resonance line to be expected for Cu-Ge alloys. To obtain agreement with experiment he finds that the numerical factor needed is 1.5. In other words the field gradients given in Table III are too small by this factor. We consider this to constitute very good agreement in view of the approximations made in our calculation.

Further corroboration of the general correctness of the theory is provided by a simple analysis of the totality of Rowland's data dealing with 14 different solutes. The experimental results for a given solute and different concentrations can be phenomenologically accounted for by the assumption that all Cu nuclei which are within a critical distance R of a solute atom do not contribute to the resonance signal. If we denote the number of lattice sites within the radius R by n, this leads to the following concentration dependence of the intensity

$$I=I_0(1-c)^n, \tag{5.1}$$

where c is the atomic concentration of solute (see Fig. 3). Rowland has presented his results in the form of

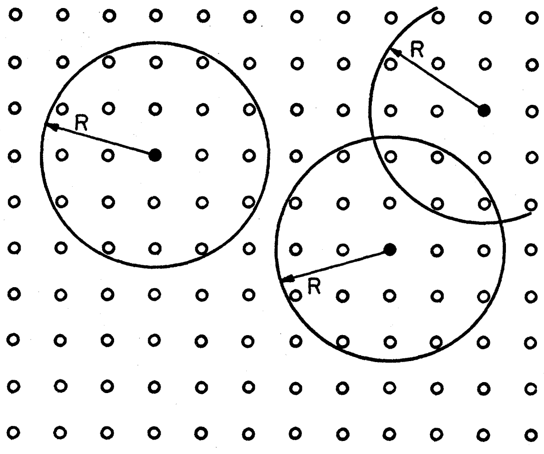

FIG. 3. Critical radius.

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[12] Anti-shielding plays a minor role for the value of α. If it were neglected α would be about 20% smaller.

TABLE IV. The number of affected copper nuclei and corresponding value of q_0.

Solute	n	q_0 in 10^{23} cm^{-3}
Ag	25	0.35
Au	48	0.38
Mg	23	0.78
Zn	17	0.88
Cd	34	0.61
Al	27	0.84
Ga	36	0.77
In	48	0.50
Si	61	0.87
Ge	62	0.85
Sn	67	0.67
P	75	0.79
As	80	0.76
Sb	87	0.70

giving a value of n for each solute. His values are given in Table IV and show a striking correlation between n and the valence difference Z'. This fits in well with the present theory according to which the amplitude A of the charge fluctuation and hence of q is also strongly correlated with Z' (Table I). On the contrary there are only minor correlations between n and the strain produced by the solute, which shows that strain fields cannot be primarily responsible for the electric field gradients in the vicinity of the solute atom.

To make these considerations somewhat more quantitative, let us adopt the following simplified picture. We assume that a shell in which q exceeds a certain critical q_0 does not contribute to the line. Thus Rowland's n is given by

$$n=\sum_{\substack{s\\(q>q_0)}} n_s, \tag{5.2}$$

where n_s is the number of atoms in the shell's. Using our Table III we can then plot n as a function of q_0. For Ge this is the step function shown in Fig. 4. A somewhat more realistic dependence is obtained by smoothing this curve. We can now take the values of n given by Rowland and thus obtain an empirical value of q_0 for each solute. This procedure gave the results for q_0 listed in Table IV. From its definition q_0 should be independent of the solute, and the moderate variation of q_0 derived from the theory is a further confirmation of its validity. Dr. Rowland has suggested that the large deviations of q_0 in Table IV which occur for Ag, Au, Cd, and In may be correlated with the relatively large cores of these elements. It is also not surprising that the deviations are largest for small values of Z'. For here our theory developed for sites far from the solute atom, is least reliable and the effects of strains, which we have neglected, must be expected to play a relatively larger role.

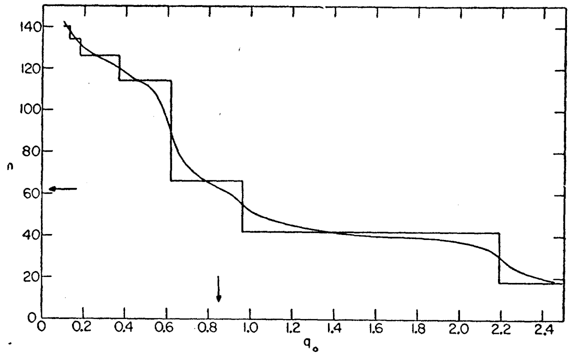

FIG. 4. Plot of number of affected nuclei n versus q_0 for Ge and Cu.

It may be worth remarking that for example in the case of Sb, the last shell of Cu-nuclei, the seventh, which experiences a significant field gradient, lies between the fourth and fifth node of the charge density fluctuations.

6. CONCLUSION

The good agreement between our theory and the large body of Rowland's data seems to us to be a strong confirmation of the reality of electron density fluctuations in the vicinity of a solute atom embedded in a metal. These fluctuations are a consequence of a discontinuous drop at the Fermi surface of $n(\mathbf{k})$, the occupation probability of the conduction band function with wave number $\mathbf{k}$. In an independent electron model there is of course such a discontinuity at zero temperature, and its small spreading at room temperature is insignificant for our purposes. On the other hand the very meaning of a Fermi surface for a gas of interacting electrons is not yet entirely clear. Rowland's experiments are therefore of special interest in providing an upper limit to a possible width of the many electron Fermi surface. Quite general considerations show that if this width in $\mathbf{k}$ space is Δk, the amplitude of the oscillations is decreased for large r by an extra factor $e^{-(\Delta k)r}$. Using Rowland's data for Sb in which effects on the Cu nuclei in the sixth or seventh shell are found for which $r\approx 9(k^0)^{-1}$, we conclude that

$$\Delta k<0.1k^0. \tag{6.1}$$

Thus we see that in response to an electrostatic field, the Fermi surface appears as quite sharp.

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