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CHARGE DENSITY OSCILLATION AROUND IMPURITIES
IN DILUTE COPPER - BASED ALLOYS

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BUDAPEST

THE ASYMPTOTIC REGION OF THE CHARGE DENSITY

OSCILLATION AROUND IMPURITIES IN DILUTE COPPER-BASED ALLOYS

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SUMMARY

The wipe-out number for the first order quadrupole effect in the magnetic resonance of the matrix nuclei was measured in dilute copper-based alloys to study the asymptotic behaviour of the charge density oscillation around different impurities. The measured values are: Cu-Zn 490 + 25; Cu-Au 880 + 40; Cu-Ni 1250 + 125; Cu-Pd 1200 + 100; Cu-Pt 1900 + 100.

For the non-transition metal impurities the experimental values were compared with the predictions from Friedel's oscillation theory by using phase shifts calculated by the Blatt, Kohn-Vosko, Alfred-Van Ostenburg, Hurd-Gordon and the pseudo-atomic methods.

For the transition metal impurities the phase shifts evaluated by Béal-Monod were used. Assuming resonance scattering for these impurities, the $\ell = 2$ phase shift was evaluated from the measured first order wipe-out number. This number was also used in combination with the impurity resistivity and the Friedel sum rule for calculating the η_0, η_1 and η_2 phase shifts for the transition metals.

The experimental values obtained in the asymptotic region give lower extrapolated charge density oscillation at the first and second neighbours of the impurity than that inferred by Rowland from the second order quadrupole effect and measured directly through satellite detection by Redfield and Schumacher et al.

РЕЗЮМЕ

В разбавленных сплавах на медной основе были измерены числа "уничтожения" при квадрупольном эффекте первого порядка в магнитном резонансе ядер матрицы для исследования асимптотического поведения осцилляции электронной плотности в окрестности различных примесей. Полученные числа уничтожения – Cu-Zn 490+25; Cu-Au 880+40; Cu-Ni 1250+125; Cu-Pd 1200+100; Cu-Pt 1900+100.

Экспериментальные данные, полученные для примесей непереходных металлов сравнивались со значениями, предсказанными исходя из теории осцилляции Фриделя с использованием значений фазовых сдвигов, вычисленных методом Блатта, Кон-Воско, Альфреда-ван Остенбурга, Гурда-Гордона, а также методом псевдо-атома.

В случае примесей переходных металлов были использованы фазовые сдвиги, вычисленные Беал-Монодом. С учетом резонансного рассеяния при этих примесях, фазовый сдвиг $\ell = 2$ был оценен из измеренного числа "умножения" первого порядка. Это число было также использовано в сочетании с примесным сопротивлением и правилом сумм Фриделя для вычисления значений фазовых сдвигов η_0, η_1 и η_2 при переходных металлах.

Экспериментальные данные, полученные в асимптотическом диапазоне, приводят к более малым экстраполированным значениям осцилляции электронной плотности на месте первичных и вторичных ближайших соседей примеси, чем значения осцилляции, предполагаемые Роуландом из квадрупольного эффекта второго порядка и измеренные непосредственно путем детектирования сателлитов Редфильдом и Шумахером и др.

INTRODUCTION

Quadrupole-perturbed NMR spectrum in high magnetic field

Let us first recall the formulation /e.g. [1]/ of the shift in the quadrupole-perturbed NMR spectrum of atomic nuclei having spin I in non-cubic lattice sites in the presence of a high external magnetic field. For an axially symmetrical electric field gradient $/q \neq o; \quad \eta \equiv 0/$ the first order shift of the resonance line is given by

$$\nu_m^{(1)} = \frac{1}{2} \left(m - 1/2 \right) \nu_Q \left(3 \cos^2 \theta - 1 \right) ,$$

and the second order shift of the central component $/m = 1/2 \longleftrightarrow -1/2$ transition/ is

$$\nu_{1/2}^{(2)} = \frac{\nu_Q^2}{16\nu_o} \left(a - 3/4 \right)\left(1 - \cos^2\theta \right)\left(9 \cos^2\theta - 1 \right),$$

where m is the magnetic quantum number, θ is the angle between the symmetry axis of the field gradient and the external magnetic field, ν_o is the Larmor frequency, $a = I/I + 1/$, $\nu_Q = 3 e^2 qQ/2I(2I-1)h$; e is the elementary charge, h is the Planck constant, q is the electric field gradient and Q is the nuclear quadrupole moment.

Electric field gradient due to charge density oscillation around the impurity

According to the Kohn-Vosko [2] and Blandin-Friedel [3] theory, the z component of the electric field gradient at the matrix nuclei around the impurity in metals of cubic symmetry can be expressed as a function of the distance r from the impurity, in the form

$$q = \frac{8\pi}{3} \alpha \Delta n(r),$$

where α is an enhancement factor accounting for both the Bloch character of the conduction electrons and the Steinheimer antishielding factor [4] and has been evaluated for Cu as 25,5 [2]. The electric field gradient is directly related to the charge density oscillation around the impurity, expressed by the asymptotic form /see [5]/

$$\Delta n(r) = \frac{A}{r^3} \cos\left(2k_F r + \varphi\right)$$

$$A \sin\varphi = \frac{1}{2\pi^2} \sum_{\ell} (-1)^{\ell} (2\ell + 1) \sin^2\eta_{\ell}(k_F)$$

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

where k_F is the Fermi wave number, and $\eta_{\ell}/k_F/$ is the phase shift of the scattered partial wave characterized by the quantum number ℓ at the Fermi energy. The phase shifts satisfy the Friedel sum rule

$$\Delta Z = \frac{2}{\pi} \sum_{\ell} \left(2\ell + 1\right) \eta_{\ell} \left(k_F\right),$$

which is the condition of self-consistency for the scattering potential. The methods used for the evaluation of the phase shifts will be considered later.

For transition metal impurities the Friedel-Anderson theory [6,7] leads to the same expressions as given above, provided that the distance between the Fermi level and the virtual level is great and that the screening charge receives contributions from states of different symmetries. If the virtual level is close to the Fermi level, resonance scattering /i.e. the term $\ell = 2$/ becomes dominant and, in accordance with the Friedel sum rule, the phase shift will be $\eta_2 = \frac{N\pi}{10}$, where N is the number of d electrons.

Lattice deformation caused by impurity /"size effect"/

The contribution from lattice deformation appears first in terms of the continuum model of solids, in the form of the Blatt correction [8]

$$\Delta Z' = \Delta Z - \frac{3}{\gamma_E} \frac{1}{a} \frac{da}{dc} Z_0 \quad,$$

where $\gamma_E = 3 \cdot (1-\sigma)/(1+\sigma)$; σ is the Poisson ratio, $da/dc \cdot a$ is the relative change in the lattice constant per unit impurity concentration, and Z_0 is the charge of the matrix ions.

The contribution to the electrical field gradient from the lattice deformation caused by impurity is given by Sagalyn et al. [9] as

$$q_\lambda = \lambda \, \frac{27}{2^{3/2}\pi \, \gamma_E} \, \frac{1}{a} \cdot \frac{da}{dc} \, r^{-3}$$

where c is the impurity concentration, and λ is an empirical parameter representing the ratio of the field gradient measured at the nuclear site to that predicted from the point charge model summed over the first neighbours. The meaning of λ is discussed more fully in an earlier report [10]. The estimation of an upper limit for λ will be considered later.

We should mention also the theory of Béal-Monod and Kohn [11], a comprehensive theory of lattice deformation which accounts for both the Blatt and Sagalyn effects and also determines the validity of the Blatt correction.

Methods for the determination of phase shifts

Table I summarizes the methods reported in the literature for the determination of phase shifts . For each method the table refers to the pertinent theoretical formula, the measured quantity used in the semi-empirical method, the type of phase shift, and the quantities which can be interpreted from the phase shifts. The values of the phase shifts obtained through these methods are specified for the different dilute alloys. For the relations of impurity resistivity and the Knight shift see [2], [12].

Reported experimental data and their consequences

Rowland [13] systematically studied the effect of non-transition metal impurities in dilute Cu-based alloys and measured the wipe-out number of the second order quadrupole effect for impurity concentrations from about 0,5 to 12 at.%.The measured values vary between 18 and 82 and are higher by a factor of 1.5 than the values calculated from the charge density oscillation using the Kohn-Vosko phase shifts.

Sagalyn et al. [9] reevaluated Rowland's data, taking into account the contribution to the field gradient from lattice deformation. Their experimental value of the parameter λ , which is $|\lambda| = 15$ or 6.7 , depending on the sign of the field gradient, is much higher than that obtained from experiments which directly measure λ /e.g. [10]/.

Among transition metal impurities the measurements on Cu-Ni, Cu-Pd and Cu-Pt only will be mentioned [14] ; for these the wipe-out numbers for the second order effect were also found to be 1.5 times higher than the theoretical values.

TABLE I.

Methods of phase shift determination

Method	Friedel sum rule	Blatt correction	Other relations	Semiempirical method			Phase shifts						Quantity evaluated from phase shifts			Remark
				Impurity resistivity	Knight shift	Field gradient	η_0	η_1	η_2	η_3	η_4	η_5	Impurity resistivity	Knight shift	Field gradient	
Pseudo atom	+	-	+	-	-	-	+	+	+	+	-	-	+	+	+	
Blatt	+	+	+	-	-	-	+	+	+	+	-	-	+	+	+	
Kohn and Vosko	+	-	-	+	-	-	+	+	-	-	-	-	O	+	+	
Hurd and Gordon	+	+	+	+	-	-	+	+	+	+	+	+	O	+	+	Non-transition metal impurity
Alfred and Van Ostenburg	+	-	+	+	-	-	+	+	+	+	+	-	O	+	+	
Béal - Monod	+	+	-	+	-	+	+	+	+	-	-	-	O	-	+/O#	Transition metal impurity

+ indicates that the quantity is used in the interpretation; - that the quantity is not used;

O indicates that the quantity is used in the semi-empirical method; # Field gradients are obtained using the measured first or second order wipe-out numbers.

Apart from in the experiments reported in our earlier papers [15,16], the first order quadrupole effect has not been measured so far on dilute Cu-based alloys.

Conclusions

The data on the second order quadrupole effect have mostly been referred to in the literature simply as quadrupole effect data /e.g. [17]/ and this has led to an erroneous estimation of the perturbation range attributed to impurities. Because of the similar magnitude of the "size" and "charge" effects the analysis of the quadrupole effect has not been considered to be as useful a method for the study of the impurity-induced perturbation as the measurement of the impurity resistivity [18]. In addition, the parameters of the field gradient measured in the immediate environment of the impurity are compared with the theoretical predictions by using asymptotic formulae.

It is clear, however, that analysis of the first order perturbation should give useful information, because the effect can reasonably be expected to have a longer range and therefore must affect a larger number of matrix nuclei than the second order effect. Thus the first order perturbation is nearly independent of the phase of the charge density oscillation; it yields information about the asymptotic region; and its comparison with the predictions from the asymptotic theory seems to be more justified. Finally, it more readily permits the investigation of very dilute alloys than the second order effect, and thus the picture extrapolated to unit impurity better reflects the true state of things.

Measurement of the first and second order effects implies the sampling of two regions lying at different distances from the impurity. Thus it can be expected that the analysis of the asymptotic behaviour will offer some explanation for the discrepancy between theory and experiment in the pre-asymptotic region when only the second order quadrupole effect is considered.

EXPERIMENTAL

The measurements were made using a field-modulated wide-line NMR spectrometer [19,20] with a resolving power of $\sim 10^{-5}$; stability of the signal amplitude, as is apparent from the experimental data, was better than 1%.

For measurements at other than room temperature a gas flow temperature controller was used, which kept the temperature stability at $\pm 0,1^{\circ}C$ and a homogeneity within the sample of better than $1^{\circ}C$.

For the detection of low intensity signals the spectrometer sensitivity was improved by a time-averaging technique. Using the NTA-512 multichannel analyzer as a coherent detector, the signal-to-noise ratio increases as $\sqrt{N}$, where N is the number of NMR signals recorded and summed true to phase in the analyzer memory.

SAMPLES

Cu-Zn   The Zn^+ impurity, with +1 excess valence, is the best available model of a point charge +e in a free electron gas. The lattice deformation caused by the impurity is small / $1/a \cdot da/dc = 0.056$, where a is the lattice constant and c the impurity concentration/. Zn is well soluble in Cu.

Cu-Au   Au has the same valence as copper. The lattice deformation it induces /0.13/ is considerable. As Au is an immediate neighbour of Pt, the Au-Pt pair can yield important information on resonance scattering at the virtual level. Au is well soluble in Cu.

Cu-Ni,   Cu-Pd,   Cu-Pt   The impurities belong to the same column of 3d, 4d and 5d transition metals and are typical representatives of non-magnetic transition metal impurities in the temperature range covered by the investigations. The lattice deformations from Ni to Pt are -0,026, 0.091, 0.101, respectively.

Specimens composed of 15-20µ thick annealed foils were used /for details see [21]/. They were prepared from either 99.998 at,%./American Smelting and Refining Company/ or 99.999 at.%. /Johnson Matthey/ grade copper by induction smelting. The homogeneity of the master alloy was checked by metallography. The purity grades of the diluents were Zn 99,95; Au 99,9; Ni Johnson Mathey; Pd 99,9; Pt 99,99 at.% /graded by manufacturer, with minimum ferromagnetic contamination/. After appropriate dilution of the master alloy, the specimens were cold-rolled to about 50% deformation and heat-treated at 250-300°C for two hours in the same atmosphere as that of the last annealing to obtain, as nearly as possible, isotropic crystallite orientation. Iron contamination was removed from the surface by etching after each rolling and cutting operation. The last rolling was followed by NMR test and a subsequent final annealing. The annealing parameters and other data are listed in Table II.

It should be noted that protective gas was used in the preparation of Cu-Zn to prevent Zn evaporation and hydrogen was added to inhibit surface and any internal oxidation.

TABLE II.

Technological data of dilute copper-based alloys

Alloy	Material	Impurity concentration at%		Analysis	Annealing paramters		
					Atmosphere	Tempe-rature	Duration hours
Cu ref. sample	99,999 at% Johnson Matthey	–		from the catalog	High vacuum	600°C	6
Cu – Zn	99,998 at% ASRC	0,031 ± 0,002; 0,214 ± 0,009; 3,37 ± 0,2; 12,54 ± 0,2	0,102 ± 0,005; 6,00 ± 0,2;	Spectrophotometry	80 % Argon + 20 % Hydrogen	600°C	6
Cu – Au	99,998 at% ASRC	0,014 ± 0,001; 0,14 ± 0,01 1,44 ± 0,07;	0,036 ± 0,002; 4,69 ± 0,07		High vacuum	500°C	5
Cu – Ni	99,998 at% ASRC	0,03 ± 0,005; 0,39 ± 0,02 6,03 ± 0,05;	0,12 ± 0,01 12,05 ± 0,05			500°C	5
Cu – Pd	99,998 at% ASRC	0,066 ± 1,5; 0,548 ± 0,5; 2,19 ± 1;	0,185± 0,5 1,15 ± 1 6,46 ± 1			500°C	5
Cu – Pt	99,998 at% ASRC	0,010 ± 0,001; 0,081 ± 0,005; 1,0 ± 0,1;	0,036 ± 0,002; 4,4 ± 0,1			500°C	5
Cu – Pt	99,9998 at% Koch-Light	0,0055± 0,0003; 0,012 ± 0,001; 0,046 ± 0,003	0,0088 ± 0,001 0,017 ± 0,001			500°C	5

Specimens for the second Cu-Pt series were prepared with extreme care from 99,9998 at.% grade Koch-Light copper.

EXPERIMENTAL RESULTS

The measured values are given only where they are thought necessary for the understanding of the asymptotic behaviour of the charge density oscillation around the impurity, or, in the case of the second order effect, for comparison with data from the literature. Since the NMR spectra which are not interpreted are not given, it should be noted that in the region of first order quadrupole perturbation /e.g. at low concentrations/ the second moment M_2 /defined in [1] / increases linearly with increasing concentrations. For the Zn-Pt series the slope of each M_2 vs c curve exhibits a similar increase to that of the wipe-out numbers.

The peak-to-peak amplitudes of the derivative NMR signal showed an anisotropy of a few per cent because of the texture of the foils. The results given are averages of values measured in different crystallographic directions.

A pure copper specimen was used for reference and the ^{27}Al line of an Al foil was measured as the marker signal along with all specimens. As the same Al foil is used for each sample and the ^{63}Cu and ^{27}Al lines are taken simultaneously, there is no need to change the sample for normalization, and thus the accuracy of the peak-to-peak amplitude measurement is better than 1%. The measured amplitudes are normalized to copper of the same purity as that used for the preparation of the alloy.

Each specimen was also measured after cold rolling. The dislocation density of the deformed specimen has a remarkable influence on the spectrum shape; it decreases the signal amplitude, and its contribution to the second moment is substantially larger than that from point defects. Here we refer to our report on the Al-Ta alloy [22]. The results not discussed here, similarly to those reported for Al-Ta, called our attention to the fact that the impurity first order quadrupole effect cannot be analysed on non-annealed samples.

Let us, then, consider three typical results.

1. The first and second order regions

The second and first order perturbation regions cannot be separated from each other by extending the Rowland-type amplitude measurement to more dilute alloys /the second order perturbation appears in every alloy and is

at the best negligible/, since the log D/D_o vs c curve does not exhibit any break. We have therefore determined the parameters of the NMR signal width which allow the two regions to be discerned distinctly. In Fig.1. the NMR results for dilute $\underline{Cu}$-Pt are shown [15]. It is clear that there is a discontinuity in the width.
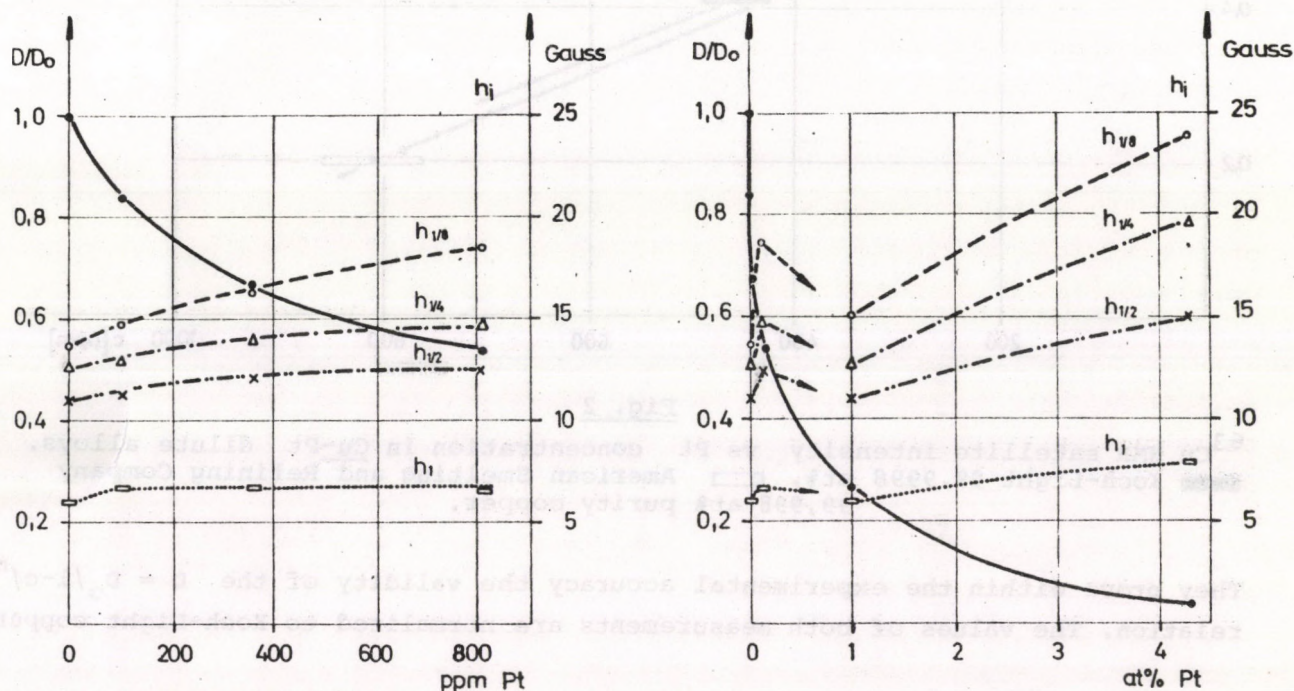

Fig. 1

Amplitude and widths of the ^{63}Cu NMR derivative signal in $\underline{Cu}$-Pt dilute alloys. The width vs Pt concentration curves are only visual aids and do not necessarily correspond to the real situation. The left-hand figure is an enlargement of the low Pt concentration side /first order quadrupole effect range/ of the right-hand one.

2. The relation $D = D_o /1-c/^n$

Special care was taken to prove the validity of the relation $D = D_o /1-c/^n$, confirmed experimentally in the second order region, in the first order region, too. The accuracy of the Pt determination, the absence of internal oxidation [23] and the good solubility prompted the use of $\underline{Cu}$-Pt for this purpose. 99,9998 at.% grade Koch-Light copper was used for the alloy and the specimens were carefully prepared.

The result obtained for this specimen is shown in Fig. 2 along with that obtained for the alloys prepared from the ASRC copper. The values specified on the ordinate are averages taken over about 100 spectra.
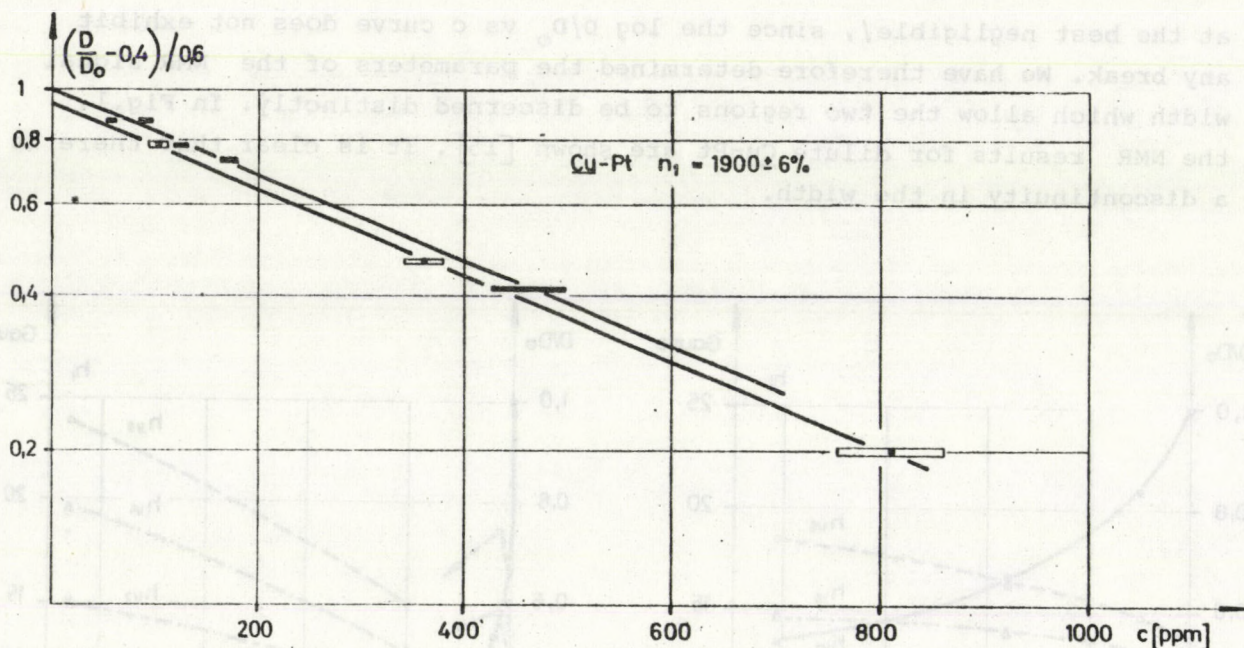
Fig. 2

[63]Cu NMR satellite intensity vs Pt concentration in Cu-Pt dilute alloys.
▬▬▬ Koch-Light 99,9998 at%, ▭ American Smelting and Refining Company
99,998 at% purity copper.

They prove within the experimental accuracy the validity of the $D = D_o/1-c/^n$
relation. The values of both measurements are normalized to Koch-Light copper.

3. The transition region

The results of the amplitude measurements on Cu-Pd shown in Fig. 3
include those for a specimen with a composition lying in the transition re-
gion. In the transition region, both perturbations have to be taken into
account and the intensity is evaluated by a linear combination of the ap-
propriately weighted wipe-out number /Brettell and Heeger [7]/ as

$$n = 0,6 \, n_1 + 0,4 \, n_2$$

More important is the observation that the measurement on the alloy in the
transition region, marked in the figure by an arrow, gives a low wipe-out
number with respect to the first order region and a high number with respect
to the second order region. The amplitude as measured peak-to-peak is inde-
pendent of the frequency at low Pd concentrations: at higher impurity
concentrations the amplitude is inversely proportional to the frequency, as
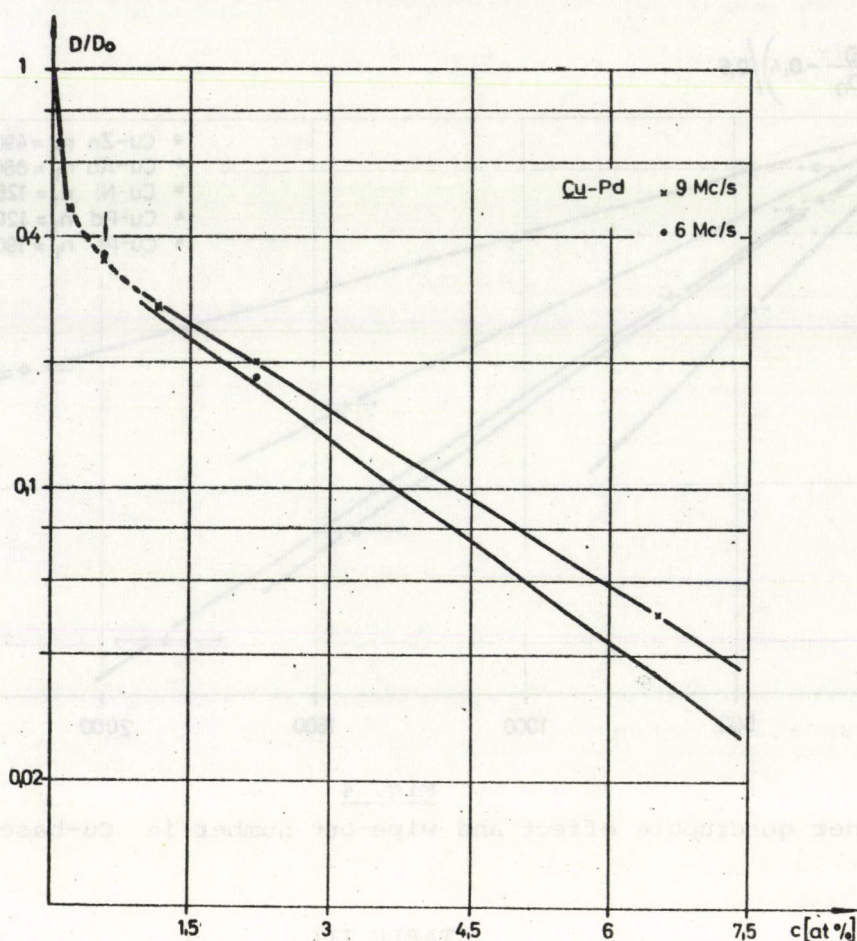would be expected for second order quadrupole perturbation.

Fig. 3.

^{63}Cu NMR intensity vs Pd concentration in Cu-Pd
dilute alloys

4. Wipe-out numbers

Let now us see the results for the first order quadrupole perturba-
tion region /shown in Fig. 4/. The series can be completed by referring
the results obtained on the magnetic Cu-Mn alloy [24]. The measured peak-
-to-peak amplitude of the derivative NMR signals are normalized to the
theoretical satellite contribution in the NMR spectrum of pure copper.
The logarithm of the normalized amplitudes is a linear function of the con-
centration. The slopes of the lines, that is the wipe-out numbers, are also
listed separately /Table III/, along with the impurity content /second com-
ponent/ of the specimens used for the determination.

The NMR spectrum parameters show no temperature dependence and are
sensitive to the magnetic field only in the second order quadrupole perturba-
tion region, as would be expected from the theory, in the temperature range
/100° - 300°K/ covered by the measurement. The relatively large experimental

$$\left(\frac{D}{D_0} - 0{,}4\right)\Big/0{,}6$$

Legend in figure:
- Cu-Zn $n_1 = 490 \pm 5\%$
- Cu-Au $n_1 = 880 \pm 5\%$
- Cu-Ni $n_1 = 1250 \pm 8\%$
- Cu-Pd $n_1 = 1200 \pm 10\%$
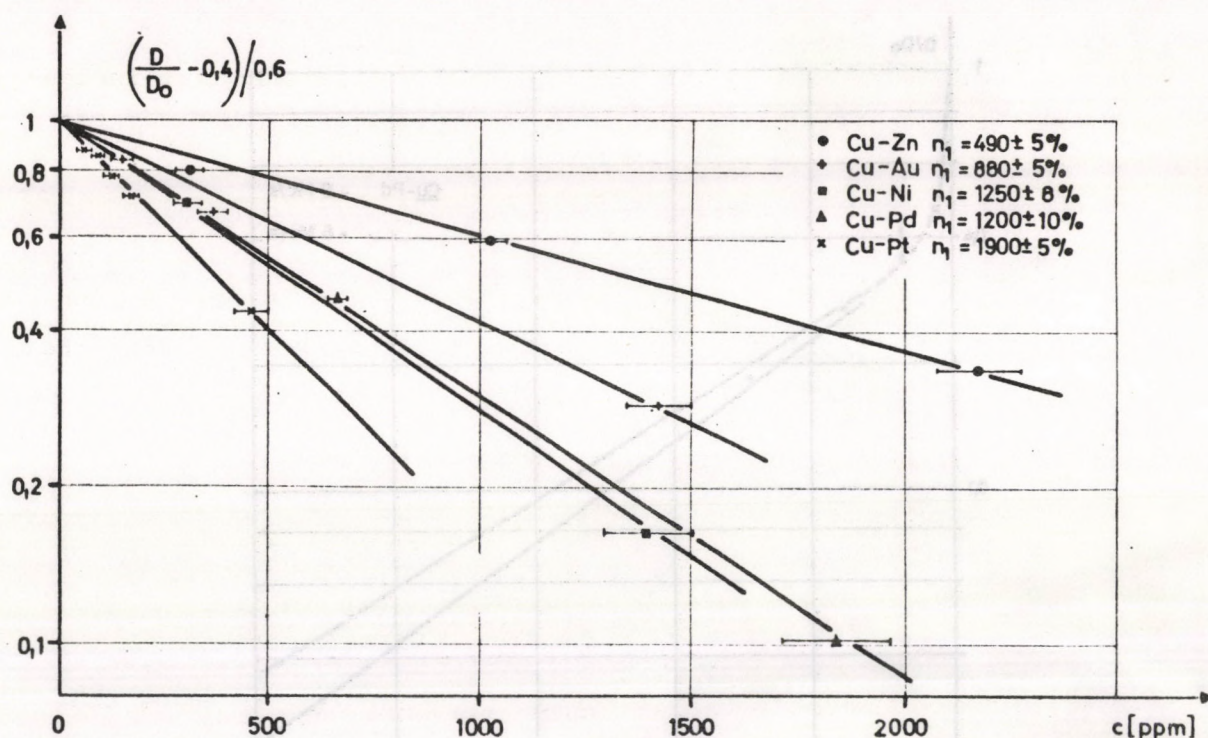- Cu-Pt $n_1 = 1900 \pm 5\%$

Fig. 4

First order quadrupole effect and wipe-out number in Cu-based dilute alloys

TABLE III

Wipe-out numbers for first order quadrupole effect in some dilute
Cu-based alloys

Alloy	Impurity concentration /ppm/	n_1
<u>Cu</u>-Zn	310 ... 2140	490 $\pm$ 25
<u>Cu</u>-Au	140 ... 1400	880 $\pm$ 40
<u>Cu</u>-Ni	300 ... 1200	1250 $\pm$ 125
<u>Cu</u>-Pd	660 ... 1850	1200 $\pm$ 100
<u>Cu</u>-Pt	55 ... 810	1900 $\pm$ 100

error of the <u>Cu</u>-Ni measurements is due to the uncertainty of the analysis.
The wipe-out numbers for the second order quadrupole perturbation /central
component/ at 6 MHz were found to be: <u>Cu</u>-Zn 17; <u>Cu</u>-Au 44; Cu-Ni 24;
<u>Cu</u>-Pd 33; <u>Cu</u>-Pt 60. It should be added that in the pairs <u>Cu</u>-Zn: Cu-Ni
/the right and left side neighbours of Cu in the periodic system/ and
<u>Cu</u>-Au : <u>Cu</u>-Pt /the impurities are neighbours/ the first order wipe-out num-

bers are 490:1250 and 880:1900, respectively. This clearly shows the exist-
ence of a virtual state in the case of transition metal impurity, an indica-
tion which is almost undiscernible by the analysis of the second order ef-
fect.

EVALUATION

In the evaluation of the experimental data it was assumed that the
field gradient and, of course, the charge density oscillation can be de-
scribed by simple Friedel oscillation.

In the first approximation - and the present evaluation should be
regarded as such - the following effects are ignored:

1/ The Sagalyn size effect. This is because in our direct measurement
   [10] $\lambda \leq 1,5$, which is only one-tenth of the contribution to the
   field gradient determined by Sagalyn et al. and thus about 10% of the
   contribution from Friedel oscillation.

2/ The Béal-Monod and Kohn [11] electron scattering by shifted matrix atoms.

3/ The theoretical refinements reported in [25], which are thought to be
   negligible in the asymptotic region.

The first and second effects cause the largest error in Cu-Au alloys.
It is still thought, however, that the evaluation introduces less error in
the asymptotic than in the second order perturbation region. The evaluation
method was the same as that described earlier [16]: essentially it is a ver-
sion of the Sagalyn method [9] adapted to the first order region.

In the first order region the wipe-out number depends only weakly
on the phase of the charge density /field gradient/ oscillation, and thus
the wipe-out number can be unambiguously related /within 10-15%/ to the os-
cillation amplitude. The enhancement factor $\alpha = 25,5$ [2] was used; the cor-
rectness of this value has been confirmed by our own measurements [10].

For better comparison, the data on the different alloys are present-
ed in tabulated form with the data on impurity resistivity [2] and Knight
shift [28] order quadrupole effect was evaluated in terms of Friedel oscil-
lation.

Dilute alloys with non-transition metal impurity

1. Cu-Zn

The results are listed in Table IV. The first order wipe-out number agrees best with the prediction from the Alfred-Van Ostenburg [26] phase shifts. The $q_{crit} = 1,8.10^{21}$ cm^{-3} calculated for these phase shifts in terms of the "all-or-nothing" model is phyiscally not illusory. The reasonable agreement with the Langer-Vosko result [29] should be noted.

Not much has to be said about the impurity resistivity. By definition it is satisfied by three systems of phase shifts. Using the Blatt phase shifts [8] the predicted value differs from the measured value crudely by a factor of 2, and in the first order quadrupole effect by a factor of 1/2. Using the Kohn-Vosko phase shifts [8], the Knight shifts measured on the smelt are overestimated to the same degree as the first order quadrupole effect. The best agreement was found also in this case with the Alfred-Van Ostenburg calculation.

Apparently, the wipe-out number calculated from the Kohn-Vosko phase shifts is much higher than the experimental value. On the other hand, the value extrapolated from the asymptotic region is lower than the field gradient measured at the first and second neighbours [30, 31].

2. Cu-Au

The results for Cu-Au are given in Table V. The agreement with the results expected from the phase shifts of Kohn-Vosko and Roberts et al. [32] is good /these latter two are the same, except that the Roberts shifts include the Blatt correction/. This is surprising if one considers that for Cu-Zn the Kohn-Vosko method yields a value exceeding the experimental wipe-out number by ∿ 70%. The pseudo-atomic phase shifts [33,34] give a correct sign for the Knight shift of the smelt, but give lower values for the impurity resistivity and the first order wipe-out number than the experimental values. This suggests that the contribution from scattering on the shifted matrix atoms is probably more important than supposed and has to be taken into account in the evaluation. The other three phase shifts do not yield the proper sign for the Knight shift. The q_{crit} calculated from the measured n_1 using the Roberts phase shifts agrees within a few per cent with the experimental value for Cu-Zn. This proves that there is no internal contradiction between the two methods of evaluation.

TABLE IV.

Data of dilute $\underline{Cu}$-Zn alloy

	Method	Phase shift					Quadrupole effect				Impurity resistivity μ ohm.cm/ at. %	Knight shift $-\frac{1}{K}\frac{\partial k}{\partial c}$
		η_0	η_1	η_2	η_3	η_4	αA	φ	n_1	n_2		
Theoretical	Langer and Vosko	-	-	-	-	-	0,60	180^0	680	-	-	-
	Blatt	0,5313	0,2410	0,0277	0,0018	-	0,19	-37^0	210	-	0,66	0,020
	Kohn and Vosko	0,521	0,35	-	-	-	0,71	$11,1^0$	800	24	+	0,273
	Hurd and Gordon	0,33078	0,24815	0,05438	0,00579	0,00039	0,23	$19,3^0$	270	-	+	0,077[++]
	Alfred and Van Ostenburg	0,203	0,254	0,059	0,014	0,004	0,42	$23,25^0$	490	-	+	0,139
Measured values									490	18	0,335	0,19

+ The quantity utilized in the semi-empirical phase shift determination method is by definition identical with the measured quantity.

++The value predicted by the Hurd-Gordon method [27] is false since it has been calculated with the constants A_ℓ and B_ℓ referring to a face-centred cubic lattice [2], instead of those referring to the smelt [12].

TABLE V.
Data on dilute Cu-Au alloy

	Method	Phase shift					Quadrupole effect				Impurity resistivity μ ohm.cm/ at.%	Knight shift $-\frac{1}{K}\frac{\partial k}{\partial c}$
		η_0	η_1	η_2	η_3	η_4	αA	φ	n_1	n_2		
Theoretical results	Pseudo atom	-0,067	0,054	0,025	-0,005	-	-0,18	0,5°	~200	-	0,11	0,013
	Kohn and Vosko	0,275	-0,092	-	-	-	0,69	-9,9°	~780	24	+	-0,249
	Roberts et al.	0,0562	-0,1951	-	-	-	0,77	-26,1°	860	-	+	-0,312
	Alfred and Van Ostenburg	-0,411	-0,020	-0,005	-0,001	-	0,48	5,2°	~550	-	+	-0,053
	Measured values								880	44	0,52	0,07

+ The quantity utilized in the semi-empirical phase shift determination method is by definition identical with the measured quantity.

Dilute alloys with transition metal impurity

Owing to the scarcity of the types and origins of reported phase shift for the Cu-Ni, Cu-Pd and Cu-Pt alloys these systems will be interpreted in a different manner from the Cu-Zn and Cu-Au alloys.

As a first step it is assumed that the observed field gradient /charge density oscillation/ originates exclusively from the $\ell = 2$ resonance scattering. The wipe-out numbers give the phase shifts for Cu-Ni as $\eta_2 = 10°5'$, for Cu-Pd as $\eta_2 = 9°55'$, and for Cu-Pt as $\eta_2 = 15°30'$, corresponding to 0,54, 0,50 and 0,86 holes on the virtual levels 3d, 4d, and 5d, respectively. This result agrees beautifully with the classical finding that there is a hole in the d-band of transition metal atoms in alloys /the number 0.6 is well known for Cu-Ni/. The result is also in good agreement with the Knight shift data for the smelt [35] and contradicts the static picture according to which the magnetization of Cu-Ni disappears at 60% Cu concentration because the s-electrons of Cu occupy the localized holes on Ni. This contradiction shows the need for a non-static interpretation of the data.

As a second step, the experimental wipe-out numbers are compared with those predicted from the Béal-Monod phase shifts [36] . It should be kept in mind that, as inferred from the wipe-out numbers of the second order effect, the asymptotic behaviour is probably less and less valid going from Cu-Pt to Cu-Ni, and that there is a discrepancy between the measured second order wipe-out numbers for Cu-Ni. The data are compared in Table VI. As with Cu-Zn and Cu-Au, the calculation based on second order data overestimates the first order experimental data for both Cu-Pt and Cu-Pd, although Cu-Ni presents an exception to this tendency.

TABLE VI.

Comparison of measured wipe-out numbers for Cu-Ni, Cu-Pd and Cu-Pt with those predicted from the Béal-Monod phase shifts

| Material | Theoretical | | | | | Wipe-out number η_1 | |
| | Phase shift | | | Amplitude αA | Phase φ | | |
	η_0	η_1	η_2			Theoretical	Experimental
Cu-Ni	0,190	-0,127	-0,260	0,95	-25°04'	1050	1250 ± 8%
Cu-Pd	-0,293	-0,120	-0,243	1,43	-16°53'	1600	1200 ±10%
Cu-Pt	-0,298	-0,008	-0,315	2,30	-18°08'	2600	1900 ± 5%

The third step is a Béal-Monod-type evaluation with the use of first order wipe-out number. The starting quantities in the semi-empirical method are the modified Friedel sum rule, the impurity resistivity and the wipe-out number for the first order quadrupole effect. The essential difference of the semi-empirical method from the Béal-Monod procedure is that the electric field gradient is related to the wipe-out number not in terms of the "all--or-nothing"model but by a method described in [16]. Essentially, Jánossy's computer calculation [37] follows the Béal-Monod pattern. The set of equations is satisfied by several triplets $/\eta_0, \eta_1, \eta_2/$; there are two for Cu-Pd and Cu-Pt and one for Cu-Ni with η_2 close to $\pi/10$, thus describing a virtually bound d state localized on the impurity.

The results showing resonance scttering are summarized in Table VII.

<u>TABLE VII.</u>

Semi-empirical phase shifts calculated from the first order
quadrupole effect

Phase shift / Alloy	η_0	η_1	η_2
<u>Cu-Ni</u>	0,221	- 0,109	- 0,276
<u>Cu-Pd</u>	- 0,046 - 0,570	- 0,171 - 0,164	- 0,262 - 0,171
<u>Cu-Pt</u>	0,168 0,792	- 0,096 - 0,072	- 0,349 - 0,188

It should be noted that the calculation for Cu-Zn alloys did not yield any solution with resonant η_2.

The results for <u>Cu-Ni</u>, <u>Cu-Pd</u> and <u>Cu-Pt</u> alloys suggest the existence of a virtually bound d state localized on the impurity. The solutions for <u>Cu-Pd</u> and <u>Cu- Pt</u> in Table VII could not be selected, in spite of the fact that the phase shifts indicate different electron states. Additional experimental data, e.g. the Knight shift measured on the smelt, may perhaps help in this respect.

CONCLUSIONS

It has been shown that the first order quadrupole effect in the NMR spectrum can be measured on dilute Cu-based alloys and can be utilized for the analysis of the asymptotic charge density oscillation around impurities in the case of simple potential scattering /for impurities of the same or of different valency as the matrix/ and in the case of scattering on virtually bound non-magnetic electronic states of 3d, 4d and 5d transition metal impurities.

We do not want to make too far-fetched inferences; too many variables are involved and the experimental data are not yet sufficient for a thorough analysis. For the time being we content ourselves with the new data obtained for some of the alloys. The final aim is, of course, the analysis of all the measurable data in order to approximate, as far as possible, the system of phase shifts consistent with all the experimental data. This would require also the appropriate refinement of the theories used for the quantitative interpretation of the data.

In the comparison with the data on the second order quadrupole effect, the first order region, which is a better approximation to the asymptotic behaviour, shows a smaller oscillation amplitude than that predicted from the second order wipe-out numbers. A trivial explanation is that in the immediate neighbourhood of the impurity the charge density oscillation is better described by the preasymptotic relations of the theory, and it is these relations which have to be used for the evaluation. It is also probable that in this region the lattice deformation is greater than the average deformation evaluated from X-ray diffraction measurements [38].

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