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Electric Field Gradients in Dilute Alloys of Copper with Nonmagnetic Transition Impurities

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Recent NMR experiments on dilute alloys of copper with nonmagnetic transition impurities can be explained if one assumes a nearly, but not completely, filled d shell on the impurity. This model gives, for the resistivities and the field gradients, theoretical results in good agreement with the experiments. The field gradients are calculated taking into account both the valency and the size differences between the impurity and the copper.

I. INTRODUCTION

The room-temperature NMR of copper atoms in several dilute alloys of copper with B subgroup elements, such as Zn, Ga, Cd, etc., has been studied by Rowland.[1] He found a rapid decrease in the intensity of the resonance line when impurities are added. This effect has been explained by the existence, at distances $\mathbf{R}$ from the impurity, of electric field gradients $Q(\mathbf{R})$ large enough to wipe out the resonance of a certain number n of copper nuclei surrounding the impurity. The theories of Kohn and Vosko,[2] and of Blandin and Friedel,[3] have shown that $Q(\mathbf{R})$ follows the oscillating variations of the electronic density due to the excess of charge introduced by the impurity. $Q(\mathbf{R})$ has the well-known asymptotic form[2]

$$Q(R)=\alpha\tfrac{8}{3}\pi A(\eta_l)\cos(2k_FR+\varphi(\eta_l))/R^3, \qquad (1)$$

where k_F is the Fermi momentum, A and φ are functions of all the phase shifts η_l, and α is an enhancement factor[2] taking into account the Bloch character of the conduction electrons and the core-polarization effects (Sternheimer factor). For impurities of the B subgroup on the *right*-hand side of copper in the classification, the η_l were reasonably assumed to be such that

$$\eta_0>\eta_1>\eta_2>\cdots. \qquad (2)$$

They were adjusted (a) to obey the Friedel sum rule

$$2/\pi\sum_l(2l+1)\eta_l(E_F)=Z, \qquad (3)$$

(Z valency difference between the impurity and the host), and (b) to the expression for the residual resistivity.[4]

$$\Delta\rho=4\pi c/Z_0k_F\sum_l\sin^2(\eta_{l-1}-\eta_l)_{E_F}, \qquad (4)$$

where Z_0 is the number of electrons per atom in the host and c, the atomic concentration in impurities.

Recent analgous experiments by Rowland and Shiotani[5] concern, now, impurities *on the left* of copper, namely: *Cu*Pd, *Cu*Pt, *Cu*Rh, *Cu*Ir (*Cu*Ni was studied previously).[1] These impurities can no longer be considered in the same framework as those referred to in Ref. 1. More generally, transition elements dissolved in noble metals posses a more or less incompletely filled d shell. For this situtation, Friedel[6] has shown that a resonance process occurs between the conduction electrons of the host and those of the incomplete d shell, leading to the existence of "virtual d bound states." Therefore, in such cases, one expects an anomalous behavior of the d phase shift:

$$\eta_2\geq\eta_{l\neq2}. \qquad (5)$$

For dilute alloys of Ni, Pd, and Pt in Cu or Au, specific-heat[7] and susceptibility[8] experiments exhibit no characteristic magnetic behavior. This should not imply that the d shell is completely filled but rather that the two half virtual d levels of the two directions of spin ↑ and ↓ are not decoupled[9] as they are in magnetic cases, *Cu*Mn, for example.

We have calculated the field gradients with the virtual bound-state model and compared them with Rowland and Shiotani's data in *Cu*Pd,[5] *Cu*Pt,[5] and *Cu*Ni.[1] We have shown, in another paper,[10] that the field gradient due to a size difference between the impurity and the host contains, actually, *two* types of terms: A nonoscillating term, proportional to the local strain (constant/R^3) as was predicted elsewhere,[11] but also, an oscillating one, anisotropic but with the same radial behavior that the contribution which would come from a valency difference. Both terms are

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[3] A. Blandin and J. Friedel, J. Phys. Radium **21**, 689 (1960).

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[5] T. J. Rowland and N. Shiotani, reported at the AIME Conference, October, 1965 and to be published; and N. Shiotani, Master's thesis, University of Illinois, 1966 (unpublished).

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[8] V. B. Svensson, Ann. Physik **14**, 699 (1932).

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[11] P. L. Sagalyn, A. Paskin, and R. J. Harrisson, Phys. Rev. **124**, 428 (1961).

only correctly described with taking into account the actual discreteness of the lattice. However, and with assuming that the monotonous part is much smaller than the oscillating one, this last contribution can be calculated in a simple way but only *approximately*, with the help of the continum theory which leads to the following correction in the Friedel sum rule:

$$2/\pi\sum_{l}(2l+1)\eta_l(E_F)=Z-(3/\gamma_E)\,\delta a/a, \qquad (6)$$

with

$$\gamma_E=3(1-\sigma)/(1+\sigma), \quad (=1.444 \text{ for a copper host}) \qquad (7)$$

and σ is the Poisson ratio, $\delta a/a$, the relative change (%) in the lattice parameter per at.% impurity. The microscopic derivation we gave[10] for (6) was shown to be exactly the phenomenological correction proposed by Blatt.[12] Therefore, *within the continum approximation*, both the size and the valency effects are included in the general formula (1), if the phase shifts obey to the modified sum rule (6).

We have explored systematically all possible sets of 3-phase shifts[13] η_0, η_1, η_2 fitting the modified Friedel sum rule (6), the experimental resistivities expressed with (4), and the experimental results concerning the field gradients. These last ones give, for each alloy, the number n mentioned in Ref. 1. On the other hand, at a given frequency, all the different n (for all the alloys which are studied) correspond to the same critical field gradient Q_0 beyond which there is no contribution to the resonance line. Moreover, Q_0 must be independent of the impurity. This unique value of Q_0 as pointed out previously,[2] should be on the order of 1.5 times the average value of 0.69×10^{23} cm^{-3} obtained by Kohn and Vosko, i.e.,

$$Q_0\simeq1.03\times10^{23} \text{ cm}^{-3}. \qquad (8)$$

We show that the set of phase shifts consistent with a virtual bound-state picture is the only one which fits the experiments fairly accurately. We find Q_0 on the order of 1.00×10^{23} cm^{-3}, corresponding to *almost one d* hole on the impurity, for each of these alloys.

We have used for $\delta a/a$ the experimental values,[14,15] and for the resistivities, the data given by Linde.[16]

TABLE I. Useful characteristics of the alloys studied in the text.

	*Cu*Ni	*Cu*Pd	*Cu*Pt
$\delta a/a$[a]	-0.026	$+0.091$	$+0.101$
Z	-1	-1	-1
$Z_{\text{eff}}=Z-(3/\gamma_e)(\delta a/a)$	-0.946	-1.190	-1.210
$\Delta\rho$ (at room temperature)[b] ($\mu\Omega$ cm/at. %)	1.25	0.89	2.1
$\Delta\rho/c$ (atomic units)	6.74	4.07	9.63
n_{exp} at 4 Mc/sec	19[c]	38[d]	60[d]

[a] Reference 14.
[b] Reference 12.
[c] Reference 1.
[d] Reference 5.

II. CALCULATION OF THE PHASE SHIFTS AND OF THE FIELD GRADIENTS IN *Cu*Ni, *Cu*Pd, and *Cu*Pt

We show in this section how we get a unique set of three phase shifts (η_0, η_1, η_2) from the modified sum rule (6), the experimental resistivities (4), and the experimental numbers n corresponding to the critical field gradients (8) which are related to the η_l by (1). The common valency difference between Ni, Pd, Pt, and Cu, is

$$Z=-1. \qquad (9)$$

We assume that

$$\eta_{l>2}\simeq0. \qquad (10)$$

Then (6) gives η_1 (for example) as a function of η_0 and η_2,

$$\eta_1\equiv\eta_1(\eta_0,\eta_2). \qquad (11)$$

Now (4) and (11) give $\Delta\rho$ as a function of η_0 and η_2 only. A CDC 3600 machine drew the curves

$$\Delta\rho(\eta_0,\eta_2)=\text{const} \qquad (12)$$

in the η_0, η_2 plane, the constant being the experimental data. These curves are closed loops and lie between two external values for η_2. In that range, to each value of η_2 corresponds two values for η_0, lying respectively, on what we will call the (a) branch of the resistivity or the (b) branch. Then the knowledge of η_2 on a specific branch implies the knowledge of only one η_0; and this couple (η_0, η_2) gives η_1 by (11).

Then we are left with only one unknown phase shift η_2 and we consider $A(\eta_l)$ and $\varphi(\eta_l)$ in (1) as functions of η_2 only.

Equation (1) can be rewritten as

$$Q(P)=135\times10^{23}\,\frac{A\cos(6.94\sqrt{P}+\varphi)}{P\sqrt{P}}, \ (\text{cm}^{-3}) \qquad (13)$$

with $P=1, 2, 3, \cdots$, referring to the 1st, 2nd, 3rd, $\cdots$, shell of neighbors from the impurity. The functions

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[12] F. J. Blatt, Phys. Rev. **108**, 285 (1957).

[13] It was *strictly impossible* to fit the experimental resistivity of *Cu*Pd (even to get the approximate order of magnitude), neither with only one phase shift (η_0 or η_2), nor with the couple (η_0, η_1) or (η_0, η_2). Therefore, we kept 3-phase shifts for *Cu*Pd, and also for *Cu*Ni and *Cu*Pt, in order to study the three alloys within the same framework.

[14] W. B. Pearson, *Handbook of Lattice Spacings* (Pergamon Press, Inc., New York, 1958).

[15] To our knowledge, there does not exist any information at the present time concerning $\delta a/a$ for *Cu*Rh and *Cu*Ir, as Rh and Ir are difficult to dissovle in Cu. Therefore, we have restricted ourselves to the three cases of *Cu*Ni, *Cu*Pd, and *Cu*Pt to adopt a consistent treatment, including Blatt's correction, for each case.

[16] J. O. Linde, Ann. Physik **15**, 219 (1932).

TABLE II. Calculated phase shifts η_0, η_1, η_2, and field gradients on the first few shells of neighbors of the impurity. Q_0 is the deduced critical field gradient corresponding to the experimental numbers n given in Table I.

	*Cu*Ni	*Cu*Pd	*Cu*Pt
η_0	$+0.190$	-0.293	-0.298
η_1	-0.127	-0.120	-0.008
η_2	-0.260	-0.243	-0.315
Q_1	5.0×10^{23} cm^{-3}	7.2×10^{23} cm^{-3}	10.08×10^{23} cm^{-3}
Q_2	1.88×10^{23} cm^{-3}	2.69×10^{23} cm^{-3}	4.05×10^{23} cm^{-3}
Q_3	0.56×10^{23} cm^{-3}	0.99×10^{23} cm^{-3}	1.45×10^{23} cm^{-3}
Q_4	0.41×10^{23} cm^{-3}	0.5×10^{23} cm^{-3}	0.78×10^{23} cm^{-3}
Q_5			0.9×10^{23} cm^{-3}
Q_0 (4 Mc/sec)	1.0×10^{23} cm^{-3}	0.97×10^{23} cm^{-3}	0.9×10^{23} cm^{-3}

Q_0 (Kohn–Vosko)$\times1.5\simeq1.03\times10^{23}$ cm^{-3} at 4 Mc/sec.

$A(\eta_l)$ and $\varphi(\eta_l)$ are explicit in Kohn and Vosko's paper.[2] For each shell, i.e., each value of P, one computes the curves $Q(P)$ as a function of η_2 only for each branch (a) and (b). Now, for a given η_2 and a given branch, one knows the values of $Q(P=1)$, $Q(P=2)$, $Q(P=3),\cdots$, for each shell of neighbors. We determine the critical field gradient in the way Kohn and Vosko[2] did (Fig. 4 of their paper,) by drawing the number of affected nuclei n versus the critical field gradients Q_0. Then plotting on these curves the actual experimental value of n given by Rowland and Shiotani (listed in Table I), we get, for each alloy, a set of Q_0 for every η_2 and each branch (a) or (b). The value of Q_0 which is closest to the value indicated in (8) will be the right one. This determines the right corresponding η_2 and the right branch; so we also know η_0 and η_1.

III. RESULTS AND DISCUSSION

1. Results

Our results for the above analysis are the following:

For *Cu*Pd and *Cu*Pt, there is only one set of 3-phase shifts fitting the Friedel sum rule modified by the size correction, the experimental resistivities, and the experimental values of n corresponding to a critical field gradient of the order of the one given in (8).[17] The phase shifts are such that

(i) they are all negative,

(ii) $|\eta_2|$ is maximum together with $|\eta_1|$ minimum

$$\text{and } |\eta_0| \text{ maximum (and } \eta_0<0). \tag{14}$$

The values of the phase shifts and those of the deduced field gradients for some of the first shells of neighbors are listed in Table II.

These results are consistent with a virtual bound-state model as described in the Introduction. The value of these phase shifts correspond approximately to

$$0.77\ d \text{ hole in } CuPd,$$

$$0.99\ d \text{ hole in } CuPt. \tag{15}$$

For *Cu*Ni we get several possible solutions. Only one is consistent with a model of virtual bound states. As such a model is well admitted for *Cu*Ni,[6,9] we deduce the set of phase shifts listed in Table II. These phase shifts are such that,

(i) η_1 and η_2 are negative, but η_0 is positive,

(ii) $|\eta_2|$ is maximum together with $|\eta_1|$ minimum

$$\text{and } |\eta_0| \text{ maximum (but } \eta_0>0),^{18} \tag{16}$$

and we get approximately

$$0.82\ d \text{ hole for } CuNi. \tag{17}$$

The result concerning the sign of η_0 is to be compared with the sign of the size correction. We note that $-(3/\gamma_\epsilon)(\delta a/a)$ in (6), (see Table I) is positive for *Cu*Ni and negative for *Cu*Pd and *Cu*Pt. It might be reasonable to think that the size difference affects essentially the s character and gives different signs for η_0 for a contraction and a dilatation.

2. Discussion

As these results depend specifically on the experimental values of the resistivities, we want to mention here that the resistivities of the alloys used by Rowland and Shiotani[5] have been checked[19] to agree with the data given by Linde.[16] The value thus found for *Cu*Pd is $0.84\mu\Omega$ cm/at.% (compared to 0.89 by Linde), and

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[17] For example, the set of phase shifts obeying to (2), which would be in favor of a complete d shell, would give a wrong result; namely, in the case of *Cu*Pd, this situation would lead to a critical field gradient of 0.3×10^{23} cm^{-3}, which is too small compared to the approximate required value of 1.03×10^{23} cm^{-3}.

[18] The set of phase shifts for *Cu*Ni obeying to the same condition (14) that for the case of *Cu*Pd and *Cu*Pt would lead to an unreasonable value of the critical field gradient 2×10^{23} cm^{-3} [compared to 1.03×10^{23} cm^{-3} given by (8)].

[19] P. Monod (private communication). We thank P. Monod for his help in measuring the resistivities of some of the samples used by Rowland and Shiotani who have kindly sent them to us.

2.03 for *Cu*Pt (compared to 2.1 by Linde) and this does not effect our results.

Yamada and Shiotani[20] have tried to go a step further in the Kohn-Vosko expansion for $Q(R)$ in powers of $(1/R)$. This expression follows as successive integrations by part of the excess electron density with respect to the energy. The $1/R^3$ term contains the phase shift $\eta_l(E_F)$ at the Fermi energy; the following term in $1/R^4$ will contain the derivative of the phase shift $[d\eta_l(E)/dE]_{E=E_F}$ and might bring a correction to (1) in the case of a virtual d bound state which has a certain extent w in energy. But so far, w remains an adjustable parameter and should be determined by other experiments. For example, the specific heat can be expressed in terms of $[d\eta_l(E)/dE]$ as Daniel and Friedel[6] have shown. But as $[d\eta_l(E)/dE]$ itself is expressed in terms of η_l and w there still remains the same number of unknown quantities.

IV. CONCLUSION

A nonmagnetic virtual bound state containing almost one d hole for Ni, Pd, and Pt in small concentration in Cu, allows satisfactory fit to the experimental resistivities and the electric field gradient of these alloys. There exist very few experimental data on dilute alloys of copper with nonmagnetic transition impurities. It could be interesting, especially in the case of *Cu*Pd [which requires absolutely the knowledge of (at least) 3-phase shifts] to study experimentally another property (specific heat, thermopower) in order to check our model of an incomplete d shell for Pd.

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[20] K. Yamada and N. Shiotani (to be published). We are grateful to Dr. Yamada and Dr. Shiotani for giving us the opportunity to read their manuscript before publication.

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Electron Paramagnetic Resonance of Gd^{3+} in YVO_4

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The EPR spectrum of Gd^{3+} in YVO_4 has been examined at room temperature with a K-band spectrometer. The results fit a tetragonal-spin Hamiltonian. The parameters are $g_{||} = g_{\perp} = 1.9916 \pm 0.0002$, $b_2^0 = -441.6 \pm 0.2$, $b_4^0 = -1.5 \pm 0.1$, $b_6^0 = 0.8 \pm 0.6$, $b_4^4 = 8.3 \pm 0.1$, and $b_6^4 = 0.0 \pm 0.2$ in units of 10^{-4} cm^{-1}. The signs of the parameters are relative.

I. INTRODUCTION

THE paramagnetic resonance study of S-state rare-earth ions (Gd^{3+}, Eu^{2+}) is basically motivated by two concerns: the character of the crystal field imposed by the host lattice and the mechanism which governs the zero-field splitting of the ground state. The latter problem has been a persistent one for some time. Recently, Wybourne[1] performed an extensive calculation to estimate the ionic contributions to the ground-state splitting of the trivalent gadolinium ion in a lanthanum ethyl-sulfate lattice. The poor correspondence between those results and experimental data suggests that the purely ionic model is inadequate, and that a correct explanation must include the detailed interaction of the ion with its ligands. Newman and Ellis[2] have considered the same ion in $LaCl_3$, and show that the observed order of magnitude of the ground-state splitting may be explained on the basis of covalency induced by spin-orbit coupling. These authors also suggest that paramagnetic-resonance measurements of the Gd^{3+} ion provide the only direct means of probing the amount of covalency in host crystals.

The character of the crystal field in this vanadate has been investigated recently by Brecher *et al.*[3] in an analysis of the polarized spectra of Eu^{3+}. The crystal has the zircon structure, and these authors find that the spectra are consistent with the D_{2d} site symmetry of the Eu^{3+} ion in this lattice. They show, that a simple electrostatic field approximation gives an adequate description of the structure of the ^{7}F multiplet, with a proviso that a more refined treatment appears to be necessary.

We report here an analysis of the EPR spectrum of Gd^{3+} in YVO_4. This work is part of a larger program devoted to the examination of the resonance spectra of rare-earth ions in the zircon structure.

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