Electric-field gradients in dilute Cu alloys: The role of the Cu *d* electrons

B. Drittler

Institut für Festkörperforschung des Forschungszentrums Jülich,
Postfach 1913, D-5170 Jülich, Federal Republic of Germany

M. Weinert

Department of Physics, Brookhaven National Laboratory, Upton, New York 11973

R. Zeller and P. H. Dederichs

Institut für Festkörperforschung des Forschungszentrums Jülich,
Postfach 1913, D-5170 Jülich, Federal Republic of Germany

The electric-field gradients induced by $3d$ and $4sp$ impurities on neighboring Cu atoms are calculated with use of local-density-functional theory and a recently developed full-potential Green's-function method. We find that the dominant contribution arises from the Cu d electrons, in particular from unoccupied antibonding d states on the Cu sites formed by hybridization with the impurity states. All previous calculations, strongly relying on jellium models, completely fail to describe this effect.

Since the pioneering work of Bloembergen and Rowland,[1] it has been realized that electric-field gradients (EFG) can yield important information about the anisotropy of the charge density in solids. Traditionally Cu alloys have been considered as a classic case, mostly because of the apparently simple electronic structure of Cu and the good solubility for many different impurities. The work of Kohn and Vosko[2] and Blandin and Friedel[3] led to a first basic understanding of the EFG as arising from the Friedel oscillations of the perturbed charge density around the impurities. Considering Cu as a nearly-free-electron material, these theories are based on a jellium model. The influence of the more-localized d electrons is described together with the core electrons by a Sternheimer antishielding factor. Using the jellium approach introduced by these authors, a large number of authors[4-11] have tried to improve these calculations by, e.g., using more accurate preasymptotic expressions for the charge-density oscillations, improvements of the impurity potentials, and a better solution of the self-consistency problem. Also the effects of lattice relaxations have been discussed in various sophistication using point-charge models together with empirical models for the displacements. In total, however, the problem of calculating the EFG remained in a rather unsatisfactory stage.

Recently Blaha *et al.*[12] have shown that the EFG can be directly calculated from the Coulomb potential using modern full-potential methods based on density-functional theory. No adjustable parameters or antishielding factors are needed. Detailed calculations of the EFG of all hcp metals[13] from Be to Cd are in very good agreement with experiments. The EFG's were found to be dominated by the anisotropic local charge density due to p states, even for those transition metals for which the d anisotropy is especially large. Blaha and Schwarz[14] and Ambrosh-Draxl *et al.*[15] have recently performed full-potential linear augmented-plane-wave (FLAPW) calculations for Cu oxide materials, where also the charge anisotropy of the d states contributes to the EFG of the Cu atoms.

The aim of our present work is to perform accurate *ab initio* calculations for the classical model system of impurities in Cu. Since all previous theoretical work[2-11] is based on jellium models, we discuss the role of the p and d electrons for the EFG in particular. A central result of our calculation is that the d electrons dominate the EFG of the nearest-neighbor Cu atoms and that for this reason jellium calculations are quite unrealistic. We give a simple explanation of this effect in terms of unoccupied antibonding d states induced by the neighboring impurities.

Our calculations rely on density-functional theory in the local-density approximation. We use the Korringa-Kohn-Rostoker (KKR) –Green's-function method[16] for point defects, which we have generalized by taking the full cellular potentials into account.[17] In a cell-centered representation, the Green's function $G(\mathbf{r}+\mathbf{R}^n, \mathbf{r}+\mathbf{R}^{n'};E)$ of the system can be written as[18]

$$G(\mathbf{r}+\mathbf{R}^n, \mathbf{r}'+\mathbf{R}^{n'};E)$$

$$= \sqrt{E}\, \delta_{nn'} \sum_L H_L^n(\mathbf{r}_>;E) R_L^n(\mathbf{r}_<;E)$$

$$+ \sum_{L,L'} R_L^n(\mathbf{r};E) G_{LL'}^{nn'}(E) R_{L'}^{n'}(\mathbf{r}';E) . \tag{1}$$

Here the vectors $\mathbf{r}$ and $\mathbf{r}'$ are restricted to the Wigner-Seitz cell and $\mathbf{r}_>$ ($\mathbf{r}_<$) denotes which of the two vectors $\mathbf{r}$ and $\mathbf{r}'$ has the largest (smallest) absolute value. As usual, $L=(l,m)$ denotes collectively the angular-momentum quantum numbers. $R_L^n(\mathbf{r},E)$ is the solution of the single potential scattering problem for a spherical wave

$j_l(\sqrt{E}r)Y_L(\hat{r})$ of angular momentum L incident on the general potential $V_n(\mathbf{r})$ of cell n. Here, $j_l(x)$ is a spherical Bessel function and $Y_L(\hat{r})$ a spherical harmonic. $H_L^n(r,E)$ is the corresponding irregular solution that, outside cell n, coincides with $h_l(\sqrt{E}r)Y_L(\hat{r})$, where h_l denotes an outgoing Hankel function. Whereas for a spherical potential both functions decouple into a radial function times a spherical harmonics, e.g., $R_L(\mathbf{r},E)=\phi_l(r,E)Y_L(\hat{r})$, for a nonspherical potential the solution can only be found by solving a set of coupled radial integral equations.[19] Details about this procedure will be published elsewhere.[17]

The structural Green-function matrix $G_{LL'}^{nn'}(E)$ contains all the information about the multiple scattering. It is related to the structural Green function $\mathring{G}_{LL'}^{nn'}(E)$ of the host by a Dyson equation. Compared to the case of central potentials treated in Ref. 16, the only difference is that for general potentials the t matrices are nondiagonal in the angular-momentum indices. In the calculations we include angular momenta up to $l=3$. In addition to the host potential, the impurity potential and the potentials of four shells of surrounding Cu atoms are calculated self-consistently.

The EFG tensor V_{ij} is given by the second derivatives of the Coulomb potential $V(\mathbf{r})$ at the nuclear position. When $V(\mathbf{r})$, the electrostatic potential of all other nuclei and all electrons, is expanded into spherical harmonics around the nuclear position

$$V(\mathbf{r})=\sum_L V_L(r)Y_L(\hat{r}) , \qquad (2)$$

the electric field gradient V_{ij} is directly determined by the quadrupolar $(l=2)$ component V_{2m} of the potential $V(\mathbf{r})$:

$$V_{ij}=\sum_{m=-2}^{+2}\widetilde{V}_{2m}(0)\frac{\partial^2}{\partial r_i\partial r_j}[r^2Y_{2m}(\hat{r})]$$

$$\text{with } \widetilde{V}_{2m}(0)=\lim_{r\to 0}\frac{V_{2m}(r)}{r^2} . \qquad (3)$$

Note that the second derivatives of $r^2Y_{2m}(\hat{r})$ are constants. If also the charge density $\rho(\mathbf{r})$ is expanded into spherical harmonics according to (2), the potential coefficients $\widetilde{V}_{2m}$ are related to the quadrupolar charge densities $\rho_{2m}(r)$ by

$$\widetilde{V}_{2m}(0)=\int_0^\infty dr'(r')^2\frac{\rho_{2m}(r')}{r'^3} . \qquad (4)$$

Typically this integral is divided into an integral over the atomic sphere $r<R$ (local contribution) and the rest (lattice contribution). The local contribution can be further analyzed according to the symmetry of the atomic wave functions. One can only have (up to $l=3$) p-p, d-d, f-f and s-d, and p-f contributions to $\rho_{2m}(r)$. Since the mixed, and in the case of transition metals also the f-f, contributions are small, the p electrons $(p$-$p)$ and d electrons $(d$-$d)$ make up most of the anisotropy of $\rho_{2m}(r)$ and hence the electric field gradient V_{ij}. According to the results of Blaha et al.,[12] core contributions can be neglected for an element like Cu at the end of the transition-

metal series. Also neglected are lattice relaxations, i.e., we fix the neighboring Cu atoms at their ideal lattice positions. The inclusion of such relaxations, while remaining a problem for the future, should not change the conclusion of this work.

Figure 1 shows the calculated quadrupolar frequencies for the first nearest neighbors of $3d$ and $4sp$ impurities in Cu. The theoretical values, obtained from (4) by using a nuclear quadrupole moment of $Q=-0.15\times 10^{-24}$ cm^2 for ^{65}Cu, agree reasonably well with the experiments. The appreciably smaller experimental values for Ga, Ge, and V could partly be due to the rather large lattice relaxations of these atoms, which are not included in the calculations. [We have also calculated the quadrupolar frequency for the nearest neighbor of a vacancy, yielding $\nu_Q=-4.1$ MHz compared to an experimental value of $(-)3.4$ MHz.[24]] In agreement with the results for hcp crystals,[13] the calculations show that the lattice contributions to the EFG are very small: typically smaller than 5% of the total values for transition-metal impurities and 5–7 % for the sp impurities. Point-charge models, which have been widely used in the literature, are therefore totally unreliable, since they consider the lattice contribution only.

The dominate contribution of more than 90% comes from directly around the Cu atom itself and can be split up into the contributions from the valence $4p$ and $3d$ electrons. Figure 2 shows these on-site p-p and d-d contributions together with the total value of V_{zz}, representing the eigenvalue of the EFG tensor with the principal axis in the direction towards the first neighbor. Clearly the d electrons, and not the p, give the most important contributions and determine the trend. This is a very surprising and unexpected result in view of all the jellium work[2–11] done on this subject. Note also that in the calculations for hcp transition metals[13] the p contributions are always more important despite the fact that in some cases the d shell has a larger anisotropy.

The physical reason for the importance of the d electrons for the EFG in Cu is the strong spatial contraction
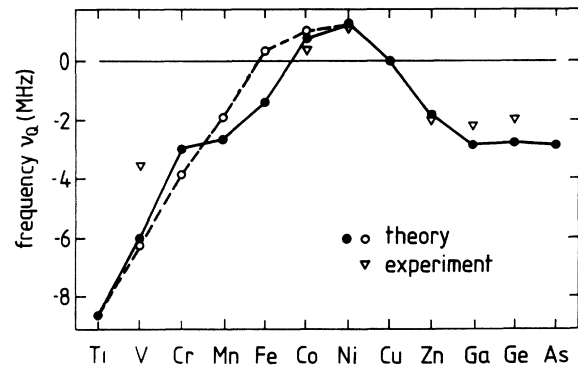

FIG. 1. Calculated quadrupolar frequencies ν_Q for the first nearest neighbors of $3d$ and $4sp$ impurities in Cu. The triangles refer to experimental data (Refs. 5 and 20–23). The sign of ν_Q has been chosen to agree with the one of the largest EFG components. The solid (dashed) line refers to a calculation including (not including) spin polarization.
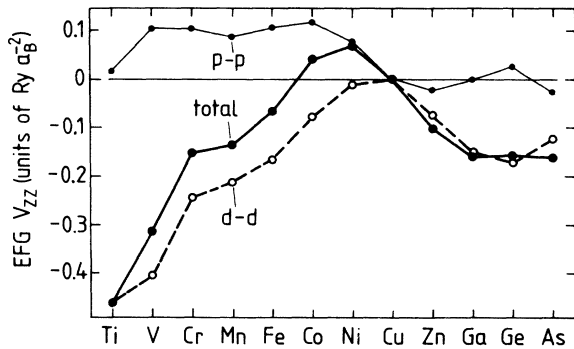
FIG. 2. Eigenvalue V_{zz} of the electric field gradient tensor of a nearest-neighbor Cu atom with principal axis towards the impurity. Shown are the d-d and p-p contributions arising from the p and d wave functions together with the total field gradient.

of the d wave functions at the end of the transition-metal series, which, due to the $1/r^3$ weighting in Eq. (4), strongly enhances their effectiveness for the electric field gradients. This contraction alone, however, is not sufficient since, e.g., in Zn and Cd the d wave functions are even more contracted but do not influence the EFG very much because they behave already as core electrons. In contrast, in Cu the d electrons still behave as valence electrons, in the sense that they hybridize sufficiently with the d or sp wave functions of the neighboring impurities. Hybridization between the host and impurity levels effectively changes the Cu d occupancy, which in turn results in nonzero contributions to $\rho_{2m}(r)$ and the EFG. For instance, the $3d$ states of the impurities form bonding and antibonding state with d electrons of the Cu d band. The virtual bound states of the impurities are essentially the antibonding hybrides[17] and contain some important d admixture on the neighboring Cu sites. Whereas for Ti the virtual bound state is far above the Fermi energy E_F and essentially fully unoccupied, for Ni it is centered about 1 eV below E_F and is practically fully occupied. Accompanying the lowering of the impurity virtual bound state is the filling of the antibonding d states on the neighboring Cu sites, which explains the trend of the d-d contributions to the EFG seen in Fig. 2 for the $3d$ impurities. For the sp impurities similar arguments hold. Here it is the hybridization between the impurity sp states and the Cu d states which creates the unoccupied antibonding-like d states on the Cu sites determining the EFG. In both cases the EFG scales with the number ΔN_d of unoccupied d states on the Cu site, provided these states are properly normalized. (Since due to the $1/r^3$ weighting only the localized atomiclike d states determine the EFG, delocalized d-like charges arising from overlap or charge transfer from the impurity should not be counted, since they are concentrated at the outer boundary of the cell and do not influence the EFG.)

The unoccupied d states can directly be seen in Fig. 3, where the anisotropic part of the charge density for a nearest-neighbor atom of a Cr impurity is plotted. Since the charge density of an unperturbed Cu atom is very isotropic (only a small $l=4$ term), the anisotropy of the charge density in Fig. 3 is induced by the impurity, located towards the left of the figure. Positive contributions
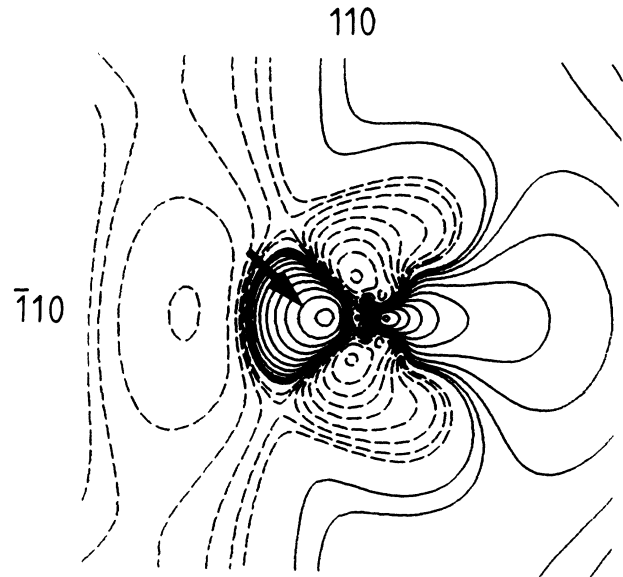

FIG. 3. Anisotropic part of the charge density of a nearest-neighbor Cu atom to a Cr impurity in Cu. Charge profiles shown for the (001) plane containing the impurity and the Cu atoms. The solid lines indicate missing charge (compared to bulk Cu), the dashed ones additional charge. The arrow points to the missing charge due to the unoccupied d states, which gives the most important contribution to the EFG. The impurity is located towards the left in $[\bar{1}10]$ direction.

are indicated by dashed contour lines, negative ones by solid lines. The arrow marks the highly directional d-hole towards the impurity, which essentially determines the EFG.

From the above discussion it is clear that jellium calculations[2-11] totally fail to describe the EFG of Cu since the Cu d states are considered as core states with fixed occupation numbers. Another indication of the failure is the anisotropy of the EFG tensor. Figure 4 shows the three eigenvalues of the EFG tensor for the directions $[\bar{1}10]$, i.e., towards the impurity, and $[110]$ as well as $[001]$, both perpendicular to this direction. In a jellium
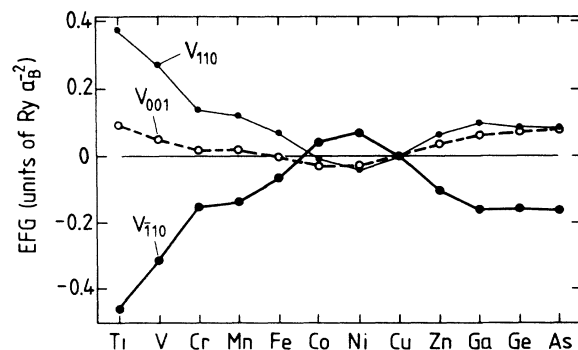

FIG. 4. The three eigenvalue of the EFG tensor of a neighboring Cu atom. The $[\bar{1}10]$ eigenvalue has its principal axis pointing towards the impurity.

model one would have $V_{110} = V_{001} = -\frac{1}{2}V_{\bar{1}10}$, since the trace of the EFG tensor vanishes. The calculations show, however, that for the $3d$ impurities the V_{001} eigenvalue is considerably smaller than the one in [110] direction, pointing to a considerable anisotropy of the charge-density disturbance around the [$\bar{1}$10] axis connecting the Cu atom with the impurity. In the past the rather large observed anisotropies have been attributed solely to size contributions arising from lattice relaxations.

Compared to the nearest neighbors, the EFG of outer-shell atoms do not have such a dominant d contribution. This can be understood from the fact that only the d wave functions of the first-shell atoms have a direct overlap with the impurity states. Since the host d states are energetically well below E_F, such d disturbances cannot propagate into the bulk, so that their effect for atoms further away is small. But also for these atoms the jellium model fails. For instance, it predicts a vanishing anisotropy of the EFG, whereas the calculated anisotropy for the third- and fourth-shell atoms is as big as the one of the first shell. (The EFG for the second shell is isotropic due to symmetry.)

In summary, we have shown that the EFG of the neighboring Cu atoms is dominated by the d electrons. We explain this surprising result by unoccupied anti-bonding Cu d states, which are formed by hybridization with the impurity states. The resulting highly directional "d-hole states" give rise to the major part of the EFG of the nearest-neighbor atoms. This effect, which cannot be described in jellium models, leads to large anisotropy factors, even if—as in the present calculations—lattice relaxations are not included.

[1]N. Bloembergen and T. J. Rowland, Acta Metall. **1**, 731 (1953); T. J. Rowland, Phys. Rev. **119**, 900 (1960).

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

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

[4]M. T. Bial-Monod and W. Kohn, J. Phys. Chem. Solids **29**, 1877 (1968).

[5]B. L. Jensen, R. Nevald, and D. L. L. Williams, J. Phys. F **2**, 169 (1972).

[6]P. L. Sagalyn and M. N. Alexander, Phys. Rev. B **15**, 5581 (1977).

[7]M. J. Ponnambalam and P. Jena, Phys. Rev. Lett. **46**, 610 (1981); Hyp. Int. **20**, 65 (1984); M. J. Ponnambalam, *ibid.* (to be published).

[8]B. Pal, S. D. Ray, S. Prakash, and J. Singh, Can. J. Phys. **61**, 1064 (1983); Phys. Rev. B **30**, 3191 (1984); Physica B+C (Amsterdam) **133B**, 210 (1985).

[9]J. Singh, S. K. Rattan, and S. Prakash, Phys. Lett. **107A**, 129 (1985); Physica B+C (Amsterdam) **144B**, 368 (1987).

[10]P. C. Schmidt, A. Coker, S. N. Ray, N. Sahoo, and T. P. Das, Hyp. Int. **31**, 69 (1986).

[11]P. Tripathi, N. C. Mohapatra, and S. Hafizuddin, J. Phys. F **16**, L161 (1986).

[12]P. Blaha, K. Schwarz, and P. Herzig, Phys. Rev. Lett. **54**, 1192 (1985).

[13]P. Blaha, K. Schwarz, and P. H. Dederichs, Phys. Rev. B **37**, 2792 (1988).

[14]P. Blaha and K. Schwarz, Hyp. Int. (to be published).

[15]C. Ambrosch-Draxl, P. Blaha, and K. Schwarz, J. Phys. Condens. Matter (to be published).

[16]P. Braspenning, R. Zeller, A. Lodder, and P. H. Dederichs, Phys. Rev. B **29**, 703 (1984).

[17]B. Drittler, M. Weinert, R. Zeller, and P. H. Dederichs, unpublished.

[18]R. Zeller, J. Phys. C **20**, 2347 (1987).

[19]A. R. Williams and J. van W. Morgan, J. Phys. C **7**, 37 (1974).

[20]G. Schnakenberg and R. T. Schumacher, Phys. Rev. B **7**, 2292 (1973).

[21]R. Nevald, B. L. Jensen, and P. B. Fynbo, J. Phys. F **4**, 1320 (1974).

[22]R. Nevald and J. Petersen, J. Phys. F **5**, 1778 (1975).

[23]D. M. Follstaedt and C. P. Slichter, Phys. Rev. B **16**, 21 (1977).

[24]M. Minier and C. Minier, Phys. Rev. B **22**, 21 (1980).