# Electric Field Gradient at $^{99}$Ru in Dilute Silver Alloys

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The quadrupolar coupling between $^{99}$Ru probe nuclei and the electric field gradient caused by the charge perturbation around fifth-row impurities (Cd, In, Sn and Sb) in silver has been investigated employing the perturbed angular correlation technique. A considerable fraction of probe nuclei is exposed to a unique electric field gradient which is attributed to the nearest neighbour probe-impurity configuration resulting from an attractive interaction. The quadrupole coupling constant increases with impurity valency. A comparison of the present results with those obtained with $^{100}$Rh nuclear probe indicates that a large probe-dependent contribution to the electric field gradient occurs, which is not related to the lattice strain induced by both probe and impurity atoms.

## Introduction

In a pure metal with cubic structure the electric field gradient (EFG) vanishes at each lattice site due to the charge symmetry. An impurity atom generally destroys this symmetry and induces an EFG at the neighbouring lattice sites. The NMR investigation of the EFG in Cu based alloys are well known (see compilation by Grüner and Minier [1], and reference cited therein). Using the NMR technique one is able to detect NMR signals from host atoms situated at different distances from an impurity and to determine precisely the EFG as a function of probe-impurity distance [2]. Probe atoms, at which the EFG is measured, and host atoms are the same and therefore one is limited to the alloys based on elements suitable for this technique.

In case of the perturbed angular correlation (PAC) technique a radioactive probe of an element in general different from alloy constituents is introduced into a dilute alloy. In contrast to the NMR investigation this technique is suitable to study the EFG on different probes in the same host-impurity system. Until now, PAC-measurements of the EFG have been performed with $^{111}$Cd [3, 4] and $^{100}$Rh [5, 6] in noble metal hosts. Here, we report on results of PAC experiments with the $^{99}$Ru probe atom in

dilute alloys of silver with Cd, In, Sn and Sb impurities. There is a special interest to use the $^{99}$Ru probe as the results can be compared with the data obtained with the $^{100}$Rh probe in the same alloys of silver. Thus one can look for a possible probe-dependent contribution to the EFG.

## Sample Preparation

Excited states of $^{99}$Ru are populated in the radioactive decay of $^{99}$Rh ($T_{1/2} = 16$ days). The radioactive $^{99}$Rh atoms were produced via the nuclear reaction $^{99}$Ru (d, 2n) $^{99}$Rh. The target consisted of about 15 mg enriched Ru powder (94% $^{99}$Ru), which was irradiated by the 15 MeV deuteron beam of the Göttingen cyclotron during 8 hours with an average beam current of 5 μA. The preparation of carrier-free $^{99}$Rh followed the method described by D. F. C. Morris and M. A. Khan [7]. The irradiated Ru powder was dissolved in $KOH/Cl_2$ in the presence of $CCl_4$. After solvent extraction of the $RuO_4$ with $CCl_4$ the remaining Rh activity was coprecipitated with $Fe(OH)_3$. The final separation of $Fe^{3+}$ by an anion-exchange process yields a solution of carrier-free $^{99}$Rh, which was almost salt-free.

As a first step of alloy preparation we made 1% alloys from inactive materials of 5 N purity. Appropriate pieces of Ag foil were melted together with Cd, In, Sn or Sb for 1 hour at 1300 K in quartz tubes filled with argon. A drop of dilute HCl containing carrier-free $^{99}$Rh was put on each alloy and on pure silver as well. The liquid was next evaporated and the samples were annealed under a hydrogen atmosphere at about 900 K for 1 hour. To get uniform distribution of $^{99}$Rh in the samples, the

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alloys were remelted. After this procedure the samples were cold-rolled to thin foils of about 50 mg/cm$^2$ in order to reduce absorption of $\gamma$ radiation. Finally, each sample was annealed under high vacuum at 800 K for 1 hour, whereafter the temperature was gradually reduced to room temperature. These alloys of 1% concentration were subsequently melted together with silver to get the less concentrated alloys of 0.3% and next 0.1% concentration. After each melting the procedure of rolling and annealing was repeated.

## Perturbed Angular Correlation Measurements

The perturbed angular correlation measurements were performed on the 90 keV 3/2 state in $^{99}$Ru. This state has a half-life $T_{1/2} = 20.5$ ns and a nuclear quadrupole moment $Q = 0.23$ b [8]. It is populated by the decay of $^{99}$Rh through the 528 keV − 90 keV $\gamma$-ray cascade (branching ratio $\approx 38\%$) with an anisotropy coefficient $A_2 = -0.22\,(2)$.

A four NaI(Tl) detector set-up and a conventional slow-fast coincidence technique were used with each detector recording the $\gamma$ radiation from both the 528 keV and 90 keV transition. Twelve different coincidence spectra $W(\Theta, t)$ of detector pairs encompassing the angles $\Theta = 90°$ and $\Theta = 180°$ were recorded simultaneously during each measurement. From the background corrected coincidence spectra the usual ratio was formed:

$$R(t) = 2 \, \frac{W(180, t) - W(90, t)}{W(180, t) + 2\,W(90, t)} . \tag{1}$$

The ratio $R(t)$ was fitted with the function $R(t) = A_2^{\mathrm{eff}}\, G_2(t)$. Here, $A_2^{\mathrm{eff}}$ is the anisotropy coefficient $A_2$ corrected with a factor which accounts for the attenuation of the anisotropy due to the solid angle subtended by the detectors and $G_2(t)$ is the perturbation factor which contains information on the EFG acting on the probe nuclei.

For a gamma-gamma cascade with the spin of the intermediate state $I = 3/2$ the perturbation factor becomes

$$G_2(t) = 0.2 + 0.8 \cos(\omega_0 t) \tag{2}$$

with $\omega_0$ depending on the EFG parameters. In the case of an axial EFG $\omega_0 = \pi \nu_Q = \pi e Q V_{zz}/h$, while for $\eta \neq 0$

$$\omega_0 = \pi \, \frac{e Q V_{zz}}{h} \sqrt{1 + \eta^2/3} . \tag{3}$$

When different probe nuclei are exposed to EFG's of different magnitudes then $G_2(t)$ depends on the distribution of both $V_{zz}$ and $\eta$. In the simple case when the fraction $f$ of probes is exposed to a unique EFG and the remaining $(1 - f)$ nuclei do not experience any quadrupole interaction the perturbation factor $G_2(t)$ is given by

$$G_2(t) = (1 - f) + f(0.2 + 0.8 \cos \omega_0 t) . \tag{4}$$

## Results

The $R(t)$ spectra obtained for $^{99}$Rh in the target material and for pure silver annealed at 570 K and 800 K are shown in Figure 1. In contrast to the spectrum for the target material the angular correlation for $^{99}$Rh in silver is very weakly perturbed. In
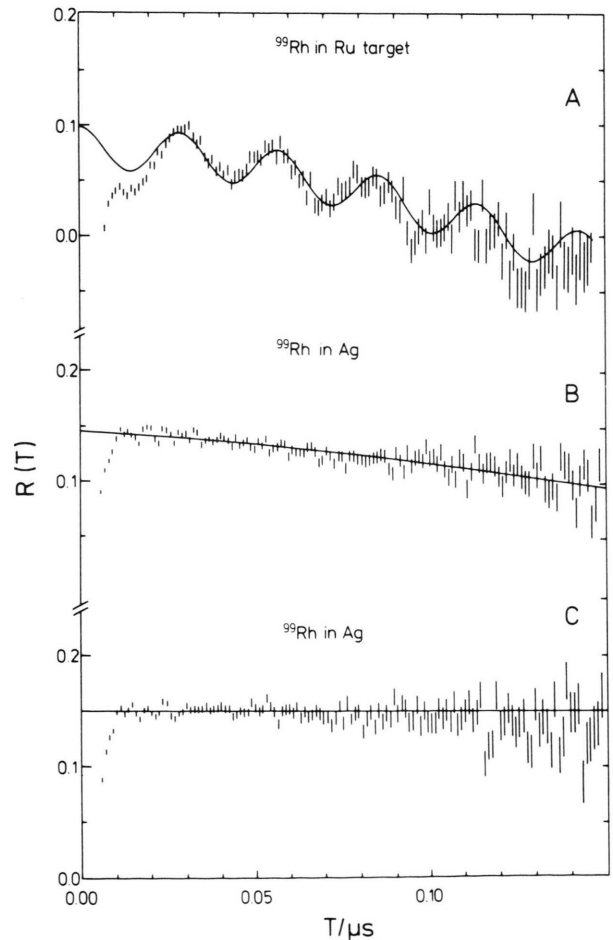


Fig. 1. PAC spectra of $^{99}$Ru after $^{99}$Rh decay. (A) $^{99}$Rh in the target material, (B) $^{99}$Rh in Ag foil annealed at 570 K, (C) $^{99}$Rh in Ag foil annealed at 800 K.

fact, the small perturbation observed for $^{99}$Rh in silver annealed at 570 K may be tentatively attributed to the quadrupole interaction due to lattice imperfections created in the sample during rolling. The lattice is fully recovered after further annealing at 800 K. This may be seen from the last spectrum where the anisotropy is constant indicating a perfect cubic charge symmetry around all probes.

The perturbation factors measured on the silver alloys with 0.3% of Cd, In, Sn and Sb impurities are
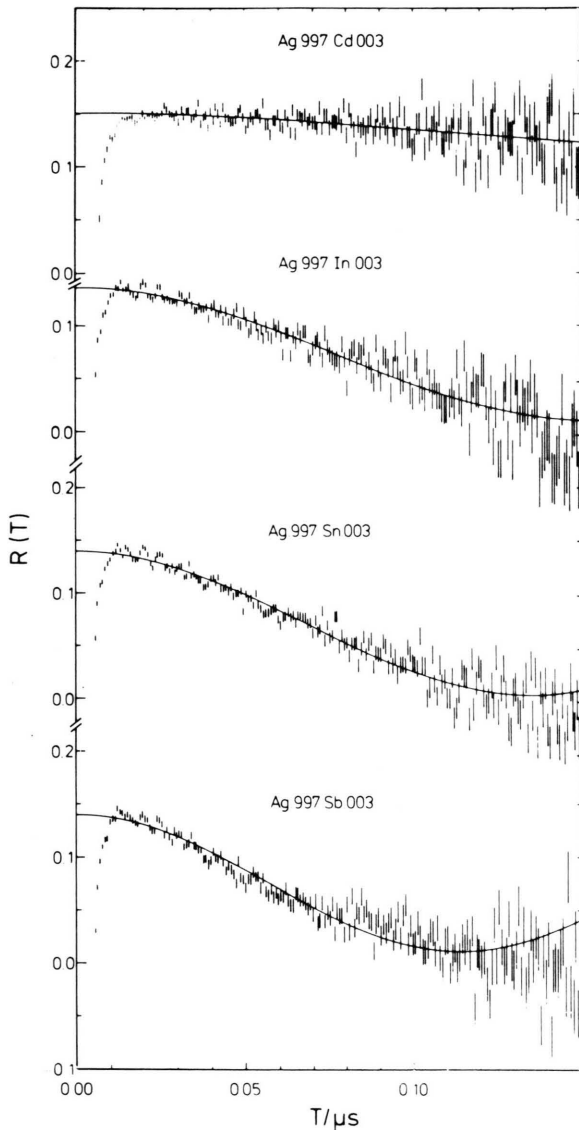


Fig. 2. PAC spectra of $^{99}$Ru after $^{99}$Rh decay in Ag$_{0.997}$M$_{0.003}$ (M=Cd, In, Sn, Sb) at room temperature. The solid lines represent least squares fits of (4) to the data.

shown in Figure 2. These spectra could be fitted with the perturbation factor for two probe-impurity configurations given by (4).

Such a result is expected at least for **AgIn** and **AgSn** alloys since the interaction between Rh and In or Sn impurities in silver based alloys is known to be attractive, creating mostly nearest-neighbour probe-impurity pairs [4, 9]. Indeed, the fraction $f$ of probe nuclei exposed to the EFG due to nearest neighbour impurity atom is much larger than that deduced for random impurity distribution, and it is large not only for In and Sn impurities but also for Cd and Sb impurities in silver.

The fraction $f$ as well as the quadrupole interaction frequency derived from least squares fits are summarized in Table 1. Using (4) to fit the $R(t)$ spectra we neglected an influence of distant impurities on the quadrupole interaction. In fact, the contribution of distant impurities may cause a small broadening of the quadrupole interaction frequency. It was found that for all alloys exept alloys containing 1% of In, Sn and Sb impurities the broadening was very small.

## Discussion

The EFG's at $^{100}$Rh probes in dilute alloys of silver was studied with the PAC technique for various sp metal impurities [5, 6]. So the reported results obtained with the $^{99}$Ru probe can be discussed emphasizing the difference of EFG parameters for different probes in the same alloy. However, the spin of the involved excited state of $^{99}$Ru is

Table 1. Quadrupole interaction results for $^{99}$Ru after $^{99}$Rh decay in Ag-based alloys at room temperature. The values $V_{zz}$ are calculated assuming the nuclear quadrupole moment $Q(^{99}Ru) = 0.23$ b and basing on the average $\omega_0$ for the alloys of a given impurity.

| Impurity | Concentration [at %] | Fraction $f$ [%] | Quadrupole frequency $\omega_0$ [MHz] | EFG $V_{zz}\sqrt{1+\eta^2/3}$ [$10^{17}$ Vcm$^{-2}$] |
|---|---|---|---|---|
| Cd | 0.3 | 17 (6) | 13 (4) | 0.86 (8) |
|    | 1.0 | 26 (3) | 15 (2) | |
| In | 0.1 | 32 (1) | 19.6 (0.3) | 1.10 (2) |
|    | 0.3 | 60 (4) | 19.1 (0.3) | |
| Sn | 0.1 | 56 (7) | 20.3 (0.8) | 1.21 (3) |
|    | 0.3 | 63 (2) | 21.6 (0.6) | |
| Sb | 0.1 | 54 (2) | 25.5 (0.5) | 1.48 (3) |
|    | 0.3 | 58 (3) | 26.3 (0.4) | |

equal to 3/2 and using this probe only one EFG parameter can be determined. From the obtained $\omega_0$ the product of $V_{zz}$ and $\sqrt{1 + \eta^2/3}$ may be derived (Equation (3)). This product is depicted in Fig. 3 together with values calculated from known [5] values of $V_{zz}$ and $\eta$ for [100]Rh probes in dilute alloys of Ag with impurities of different valence.

Obviously, the EFG's measured with [99]Ru and [100]Rh probes in the same alloy differ from each other at least for In, Sn and Sb impurities. The systematic difference may be due to different Sternheimer antishelding factors and uncertainties in the quadrupole moment values. The relative variation of $V_{zz}$ ($\sqrt{1 + \eta^2/3}$) for both probes with respect to different impurities, however, is independent of these uncertainties. Therefore one can conclude that the EFG produced by an impurity atom in a cubic metal at the nearest neighbour site depends significantly on the probe which was used for measuring.

Probe dependent contribution to the EFG may originate in the lattice distortion caused by the impurities and probe atoms [10]. The EFG measured with two probes of different size neighbouring the same impurity atom is measured, in fact, at various distances from the impurity. However, both the Ru and Rh atoms have the same atomic radius and the effect of different displacement of the first nearest neighbours to these probe atoms may be neglected.

A possible approach to understand the observed nearest neighbour EFG dependence on probe properties is to take into account different electronic structures of probes of different elements. For example, such an approach was developed to explain the extremely strong probe dependence of the EFG at sp metal probes in the hexagonal lattice of cadmium [11]. In terms of a tight binding model for the electronic structure at sp impurities [11, 12] the
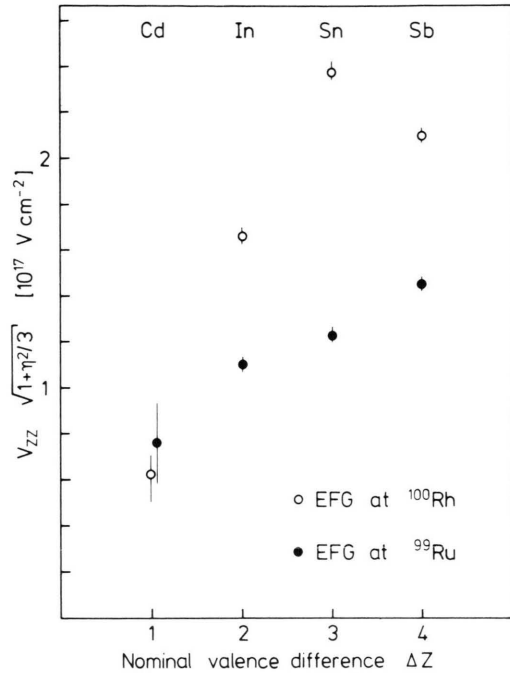


Fig. 3. Impurity-induced EFG in silver measured with [99]Ru and [100]Rh probes as a function of the nominal host-impurity valence difference (present work and [5]).

EFG varies significantly with the number of p electrons of the probe. Unfortunately, no prediction was formulated until now on the EFG at probes with partially filled d electron shell. The data for [99]Ru and [100]Rh in cubic alloys point to a probe-dependent contribution to the EFG also for probes with not-filled d shell. This contribution can not at all be related to the probe atom size. The observed trend is an increase of the EFG with the number of d electrons for more than half filled 4 d electron shell.

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