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Characterization of Copper (100) Surfaces by Isolated Indium Probe Atoms via the Electric Field Gradient

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The electric quadrupole hyperfine interaction at Cu (100) surfaces has been detected at isolated ^{111}In probe atoms by use of the perturbed $\gamma\gamma$ angular correlation technique. The electric-field-gradient tensor at $T=295$ K was found to be axially symmetric with a strength of $|V_{zz}|=1.0(2)\times10^{18}$ V/cm^2 and the symmetry axis perpendicular to the (100) surface. A linear temperature dependence of the electric field gradient was observed. These findings support the assumption of highly symmetric surface sites as positions for the ^{111}In probes.

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Surface studies utilizing nuclear methods have attracted enormous attention in the past few years. A considerable part of the efforts in this field is concentrated on applications of hyperfine techniques like NMR, Mössbauer effect, and perturbed $\gamma\gamma$ angular correlations (PAC). For this purpose, important key experiments have been reported. A first study of the electric field gradient at surfaces was performed with PAC for In (111) surfaces, where the sensitivity to growth processes has been demonstrated.[1] NMR measurements with nuclear-spin-polarized alkali-metal atoms adsorbed on W (110) surfaces were reported, yielding information on averaged electric field gradients probed by the diffusing probe atoms.[2] Most recently, Fe (110) surfaces were investigated by Mössbauer spectroscopy from which detailed information on the surface hyperfine fields has been gained.[3]

Common to the reported Mössbauer and PAC experiments are the facts, first, that only pure systems, i.e., probe and substrate atoms from the same element, have been studied and, second, that the depositions containing the probe atoms (^{57}Fe, ^{111}In) are covering most of the surface area. Both facts are severe restrictions for a more general applicability of the two methods; only surfaces of optional composition and structure *labeled* with *isolated* probe atoms open a wide field of interesting questions.

In this Letter we report on a study of the electric field gradient detected with isolated ^{111}In probe atoms on Cu (100) surfaces. The appearance of a nonvanishing electric field gradient is a property of the broken symmetry at the copper surface, since probe atoms placed substitutionally inside the Cu bulk are not exposed to any electric field gradient because of the cubic lattice structure. For the first time we have measured the exact orientation and the temperature dependence of this surface electric field gradient.

The electric field gradient acting on a probe nucleus is produced by the extranuclear charges and is dominated by the arrangement of the next-neighbor atoms. Copious information is contained in this physical quantity: The strength of the electric-field-gradient tensor is usually described by the largest component in the principal-axis system, V_{zz}, the symmetry by the asymmetry parameter $\eta=(V_{xx}-V_{yy})/V_{zz}$ ($\eta=0$: axial symmetry); the orientation of the principal-axis system with respect to the laboratory frame yields structural information; and, finally, the temperature dependence of the electric field gradient is governed by lattice vibrations. All this information is accessible through a perturbed $\gamma\gamma$ angular correlation (PAC) experiment, where only a very low number of probes (typically 10^{10}) are necessary. In our case ^{111}In was used as PAC probe; following the β^- decay of ^{111}In, the $\gamma\gamma$ angular correlation is measured for the 171–245-keV γ cascade of ^{111}Cd. Thus the interaction of the electric quadrupole moment [$Q=+0.83(13)$ b] of the ^{111}Cd nucleus in the isomeric $\frac{5}{2}^+$ state ($T_{1/2}=85$ ns) with an extranuclear electric field gradient can be observed. This hyperfine interaction perturbs the $\gamma\gamma$ angular correlation resulting in a modulation of the delayed coincidence probability between the two γ quanta. Four γ detectors, encompassing 90° with each other, are used to measure $\gamma\gamma$ coincidences, which for the different detector combinations can be compressed into the usual counting ratio $R(t)$. In the case of only one electric field gradient acting on the probe nuclei in the $\frac{5}{2}^+$ state, this $R(t)$ spectrum can be expressed as a superposition of three frequencies (for details see the work of Witthuhn and Engel[4]):

$$R(t)-A_{\text{eff}}\left[s_0+\sum_{n=1}^{3}s_n\cos(c_n\omega_0 t)\right], \tag{1}$$

with $\omega_0=3eQV_{zz}/20\hbar$ the quadrupole interaction frequency and A_{eff} an effective angular correlation coefficient. The coefficients s_0, s_n depend characteristically on the orientation of the principal-axis system of the electric-field-gradient tensor with respect to the detector plane.[5] Finally the parameters c_n depend only on the asymmetry parameter η; for $\eta=0$ one obtains $c_1=1$, $c_2=2$, and $c_3=c_1+c_2=3$.

Copper (100) surfaces were prepared either *in situ* by evaporation and epitaxial growth on air-cleaved NaCl or by use of Cu single crystals sputter-cleaned and annealed at 800 K under UHV conditions (pressure $< 10^{-8}$ Pa). The crystallographic conditions of the surfaces were monitored by low-energy-electron diffraction (LEED). Radioactive ^{111}In probe atoms were deposited onto the copper surfaces by a two-stage evaporation procedure in order to purify the deposition of activity. After reduction of the commercially available ^{111}InCl$_3$ under H$_2$ atmosphere and diffusive transport of ^{111}In onto a copper pellet, this pellet was mounted inside the UHV system. The ^{111}In-loaded pellet was then carefully heated and the ^{111}In activity was evaporated onto an out-gassed copper backing. From this copper backing the ^{111}In activity finally was evaporated onto our Cu (100) surfaces. A concentration of about 10^{-4} ^{111}In atoms on the surface was obtained. With an Auger-electron spectrometer the contamination of the surface by impurities was recorded. Nonactive In with a concentration on the order of 10^{-3} was found; this contamination stems from the production process of the ^{111}In activity. In addition C and Cl impurities were detected with concentrations in the 10^{-2} range. Annealing of the surface up to 580 K leads to a quantitative desorption of the Cl impurities.

In Fig. 1 three PAC time spectra are depicted, which were recorded for two different samples. For better illustration Fourier transforms of the experimental time spectra are shown on the right. The upper two spectra were obtained from a Cu single-crystal sample with the surface normal pointing at 45° between two adjacent γ detectors (definition of angles: see inset Fig. 2). Spectrum *a* was measured after annealing of the sample to 250 K for 20 min; in this case the Cl impurities have not yet been desorbed. After annealing of the sample at 580 K all Cl impurities have been removed and then the PAC spectrum shown in Fig. 1(b) was recorded. In Fig. 1(c) a PAC spectrum is presented for an epitaxially grown Cu (100) sample with an orientation of the surface normal perpendicular to the γ-detector plane. This sample also was annealed up to 580 K in order to remove the Cl contamination.

The two sharp frequencies which are visible in Figs. 1(b) and 1(c) are characteristic for ^{111}In probes exposed to a well-defined electric field gradient, with amplitudes depending on orientation of the sample with respect to the γ detectors [for other orientations a

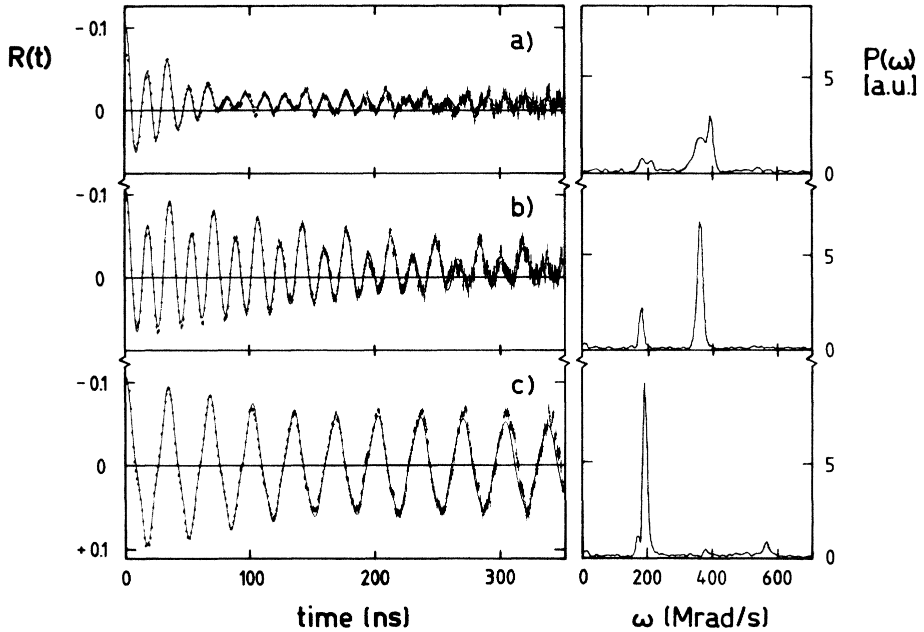

FIG. 1. PAC time spectra (left-hand side) with their Fourier transforms (right-hand side) for isolated ^{111}In probes on a Cu (100) surface. The time spectra are fitted by Eq. (1). (a) Cu single-crystal sample with surface normal oriented at $\phi=45°$, $\theta=0°$ with respect to the γ-detector plane. The surface is contaminated by Cl impurities. (b) Same as (a) without Cl impurities. (c) Epitaxially grown Cu sample with surface normal perpendicular to the γ-detector plane ($\theta=90°$). (For definition of angles see inset in Fig. 2).

third frequency can be observed as well; compare Eq. (1)]. From the measured amplitude in the PAC time spectra at $t=0$ we conclude that at least 90% of the ^{111}In probes are exposed to the same surface field gradient. The result for this surface electric field gradient at $T=295$ K is

$$|V_{zz}| = 1.0(2)\times 10^{18}\ \mathrm{V/cm^2},$$

$$\eta = 0.00(5)\ \text{(axial symmetry)}.$$

The error in the electric-field-gradient value includes the experimental error for the quadrupole moment and a few percent scattering of measured quadrupole frequencies obtained for different samples. This slight scattering of quadrupole frequencies for different samples is not yet understood.

The situation is quite different for ^{111}In probes at a Cu (100) surface still containing Cl contamination [Fig. 1(a)]. Here a considerable fraction of ^{111}In probes is experiencing an electric field gradient 9% higher than the one for surfaces without Cl impurities. This change therefore has to be attributed to In-Cl configurations at the Cu (100) surface. This result demonstrates the sensitivity of our method to observe probe-impurity pairs at surfaces, which is an important aspect for impurity diffusion studies.

As one can see from Fig. 1 the PAC spectra exhibit a strong dependence on the geometrical orientation of the sample. We have measured the amplitudes s_0 and s_n for a selected set of angles between the surface normal and the γ-detector plane. For this we have used an epitaxially grown Cu (100) surface. The result is shown in Fig. 2. For an axially symmetric electric field gradient pointing along the surface normal and pointlike sample and γ detectors the dependence of the amplitudes s_0 and s_n can be calculated[5]; this is represented by the dashed curves. The finite solid angle of our γ detectors can also be taken into account,[6] which results in the solid lines in Fig. 2. The agreement with the experimental data clearly establishes the fact that the symmetry axis of the electric-field-gradient tensor is directed perpendicular to the (100) surface. Theoretical estimates, based on point charges representing the metal ions, are only consistent with the observed orientation and axial symmetry of the electric field gradient if a configuration with fourfold symmetry with respect to the surface normal is adopted. This high symmetry suggests that the ^{111}In probes are occupying regular terrace sites at the Cu (100) surface. Since our Cu surfaces contain C impurities, the observed electric field gradient could also originate from In-C configurations; however, the orientation and high symmetry of the surface field gradient makes this explanation rather unlikely. Furthermore, we have observed that the PAC effect is independent of the C content and that at higher C concentrations (> 15%) the ^{111}In activity starts to desorb from the surface already above temperatures $T=500$ K. This hints at the fact that In-C complexes are less stable than In at Cu (100) surfaces.

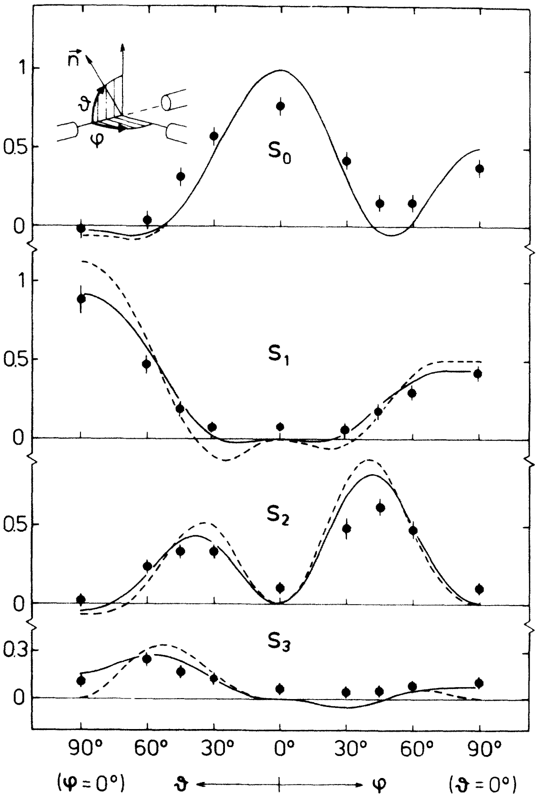

FIG. 2. Dependence of the frequency amplitudes of Eq. (1) for isolated ^{111}In probes on a Cu (100) surface as a function of a selected set of angles between surface normal and γ-detector plane. Theoretical curves for the symmetry axis of the surface field gradient perpendicular to the γ-detector plane are included; the dashed curve is obtained for pointlike sample and γ detectors, the solid curve for detectors with finite solid-angle resolution.

Another important piece of information is the temperature dependence of the observed surface field gradient. In bulk material (noncubic crystal structure) this temperature dependence exhibits a $T^{3/2}$ behavior in general and it is commonly accepted that the mean square displacements of the probe atoms and their immediate neighbors are mainly responsible for this effect.[7,8] In the case of atoms on a (100) surface of fcc crystals it is well known that an enhanced vibrational amplitude perpendicular to the surface, and therefore an anisotropic mean square displacement, occur which would influence the temperature dependence of the surface field gradient. Therefore, we have measured the electric field gradient for ^{111}In at Cu (100) surfaces in a temperature range between 77 and 570 K. The result is shown in Fig. 3; the data points are well

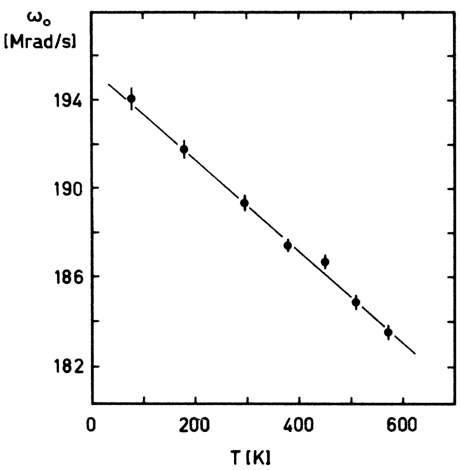

FIG. 3. Temperature dependence of the quadrupole interaction frequency observed for isolated ^{111}In probes on a Cu (100) surface. The solid line is a fit to the experimental data assuming a linear temperature dependence.

represented by a linear temperature dependence

$$\omega_0(T) = \omega_0(T=0)[1 - CT], \qquad (2)$$

with $\omega_0(T=0) = 195(1)$ Mrad/s and $C = 1.05(4) \times 10^{-4}\,\mathrm{K}^{-1}$.

Torgeson and Borsa,[9] who have utilized the nuclear quadrupole resonance technique, have found a similar result for ^{93}Nb in NbSe$_2$, which has a quasi two-dimensional structure. They have interpreted their finding within an anisotropic phonon model described by two different Debye temperatures, where the effective Debye temperature for vibrations perpendicular to the layers is taken to be smaller by a factor of about 3. This assumption leads to a rather linear dependence of the mean square displacement. The same *Ansatz* as proposed by Torgeson and Borsa can be used for our case. Although a quantitative theory for our system does not exist, it is obvious that the linear temperature dependence of the electric field gradient reflects a quasi two-dimensional phonon spectrum.

The appearance of a well-defined electric field gradient throughout the entire temperature range raises another interesting question. If one looks at known surface diffusion data[10] it is rather unlikely that the ^{111}In probe atoms are immobile at temperatures up to 570 K. Our result therefore suggests that, if ^{111}In atoms are diffusing along the surface, they are scanning surface sites with identical electric field gradients so that a quasistatic surface field gradient is observed.

In this Letter we have demonstrated that isolated ^{111}In probe atoms deposited on a Cu (100) surface are exposed to electric field gradients with unique properties. The well-defined electric field gradient can be used to study diffusion processes at surfaces on a microscopic level. Atomic species whose diffusion behavior is of interest may be trapped at PAC probes and cause a detuning of the original surface field gradient, as we have demonstrated for Cl impurities. At elevated temperatures detrapping may occur, which again can be followed via the electric quadrupole hyperfine interaction with very high accuracy. Furthermore, diffusion processes for different surface orientations of a certain material can be studied. For such investigations the electric-field-gradient tensor for the different surface orientations has to be known; experiments with Cu (110) and Cu (111) surfaces using Cu single crystals are in preparation.

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