Quadrupole Interaction at Surfaces – Nuclear Methods*

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The measurement of the electric quadrupole interaction with nuclear techniques allows the study of monolayer coverages or even isolated atoms at surfaces and interfaces due to the inherent sensitivity of these methods. Recently electric field gradients at surface atoms have been investigated with Mößbauer Spectroscopy, Polarized Beam NMR, and Perturbed Angular Correlation (PAC).

The highly sensitive PAC technique with ^{111}In and ^{111m}Cd sources, in particular, has been applied to several metal and semiconductor surfaces. The use of flat as well as stepped surfaces has allowed the assignment of the measured quadrupole interaction frequencies to specific surface sites. For the Pd(111) surface a particularly complete description is possible, since for five different sites (terrace adatoms, ledge adatoms, kink adatoms, ledge and terrace atoms) the field gradients and their orientation could be determined. They represent a challenging problem for understanding the electronic structure of metallic surfaces. Through the study of the temperature dependence of the different components the diffusion of the radioactive probe atoms can be followed.

The data from ^{57}Fe Mößbauer spectroscopy on iron surfaces with monolayer coverage and NMR surface studies of ^{7}Li and ^{23}Na at high temperatures are reviewed.

An outlook for further developments of the nuclear techniques is presented, particularly in view of the variety of radioactive isotope beams available from on-line isotope separators like the ISOLDE facility at CERN.

I. Introduction

For the study of pure surfaces or monolayer coverages many experimental methods have been developed. Very sparse data, however, exist for isolated impurities or defects on surfaces. In recent years the corresponding problem for impurities and defects in bulk metals has been attacked with the use of nuclei as probes. The typical techniques one uses for such experiments are perturbed angular correlation (PAC), Mößbauer spectroscopy (MS), or polarized beam NMR. The microscopic site can be characterized by the electric field gradient (efg), magnetic hyperfine field or isomer shift observed with these techniques. All these methods generally require a small number of probe atoms. In a typical detector one works with count rates of $5 \cdot 10^5$ events per second at a solid angle of 2%. For source halflifes of one hour this translates to 10^{10} atoms necessary for a measurement. Virtually isolated probe atoms can thus be investigated on a surface of typically 1 cm^2, certainly much less than monolayer coverages (10^{15}/cm^2).

This review of the rather young field of hyperfine interaction studies at surfaces shall be restricted to well defined surfaces and the observation of electric field gradients by nuclear techniques.

In Fig. 1 a simplified model [1] for a real surface is shown. It contains as basic building blocks atoms situated on terraces, ledges, and kinks. These sites have a different non-symmetrical atomic environment that manifests itself in different efgs that could then after proper characterization be used to study questions such as impurity site occupation at surfaces, surface reconstruction, diffusion processes, surface magnetism, chemical reactions or eventually catalysis.

The topics covered in this review are first the techniques for deposition of radioactive atoms on clean surfaces and their desorption. The methods used in the measurements of the nuclear quadrupole interaction at surfaces are then shortly described together with some representative experiments. Finally an overview of the existing data on electric field gradients at surfaces is presented, and some emerging trends are pointed out.

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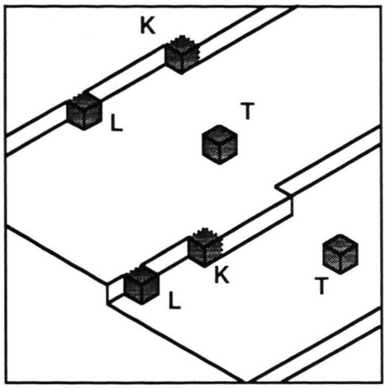

Fig. 1. Terrace-Ledge-Kink model (Kossel-Stranski).

II. Surface Techniques

The central problem in the use of radioactive atoms for studying surfaces is the sample preparation and the clean deposition of the probe nuclei on the surface.

Common techniques for the preparation of clean surfaces are sputtering and annealing, high temperature flashing to vaporize off impurities, and epitaxial growth of layers by evaporation. Cleaving under UHV conditions can also produce very clean surfaces. If one wants to go one step further and also control the surface orientation, this is usually done by carefully preparing a so-called vicinal surface, where the normal of the lattice makes a small angle to that of the surface. After proper cleaning and annealing a quite regular array of atomic steps may be formed in favourable cases. Typically in a vacuum of 10^{-9} mbar a surface is covered with a monolayer of dirt in about one hour. Thus working at 10^{-11} mbar is essential for most experiments.

How can one then bring the radioactive atoms to the surfaces that one would like to study?

IIa) On-Line Deposition

Radioactive ion beams offer the cleanest way to bring radioisotopes into a UHV system. This is possible without contamination by stable isotopes in many cases. Ion beams in the energy range of 10 to 200 keV are generally produced from isotope separators. Long-lived isotopes may be obtained from off-line separators, but the most versatile method clearly is the on-line production of the radionuclides in the ion source. Several such facilities exist, coupled to reactors, light ion or heavy ion nuclear accelerators or high energy machines [2]. The largest and most productive such separator is definitely the ISOLDE facility at CERN [3]. Due to the high energy of the primary beam, 1GeV protons, very thick targets up to several 100 g/cm^2 may be employed there. This leads to very strong sources produced. The radioactive isotopes are vaporized out of the target material, ionized (in an element specific way whenever possible), accelerated to 60 keV and mass separated in a magnetic field. Several upgrades of the facility have lead to ever more intense and cleaner beams available for a wide range of elements [4].

A procedure for depositing these radioactive atoms on surfaces has been successfully tested at ISOLDE-2 for Cd, In and Rb [5]. Since the beamline vacuum there was only in the 10^{-6} mbar range, a set of differential pumping stations was used to separate it from the ultrahigh vacuum chamber which operates in the 10^{-11} mbar range. The somewhat improvised UHV setup employed in the pilot experiments is sketched in Figure 2. The basic idea is then to implant the radioactive atoms into a pre-cleaned oven from where they can be evaporated onto a properly prepared sample. For the perturbed angular correlation measurements, in particular, four detectors are positioned outside the vacuum system near the sample site.

During the first experiments with this setup it was realized, that for deposition on very cold surfaces the simple evaporation process resulted in too much sample heating [6]. It was found that by the introduction of a two-stage deposition technique, as schematically shown in Figure 3, this problem could be eliminated. The radioactive atoms are first implanted into a molybdenum foil some 500 Å deep. From there they are evaporated at high temperature onto a precleaned second molybdenum foil. They can then be transferred to the actual sample by gentle heating.

At the new ISOLDE facility at the CERN PS-Booster [7] a beamline in UHV standard and a special surface physics chamber has been constructed and successfully tested. This Apparatus for Surface Physics at ISOLDE CERN ("ASPIC"), specially designed for operation at ISOLDE, is a versatile system for surface and interface measurements [8]. It is fully based on the indirect deposition technique developed in the pilot experiments as described above. A carefully cleaned and degased transfer foil mounted on a special transportation manipulator takes the activity into the main chamber working in the 10^{-11} mbar range.

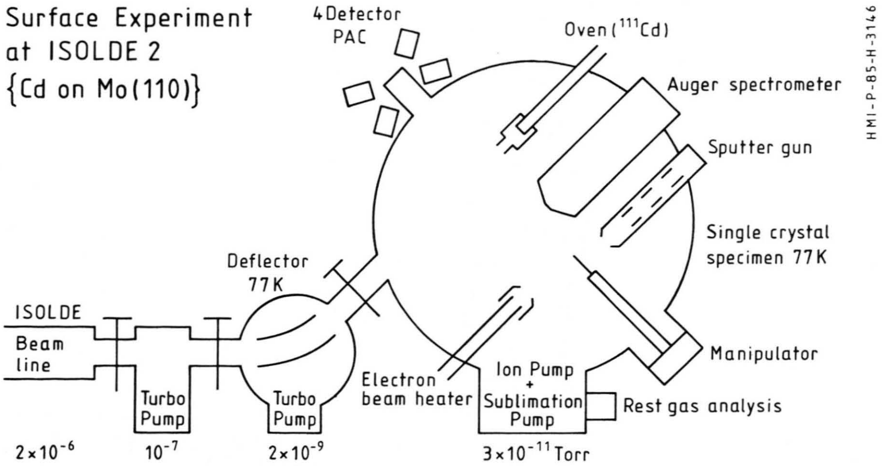

Fig. 2. Schematic layout of the surface physics chamber used at ISOLDE-2.

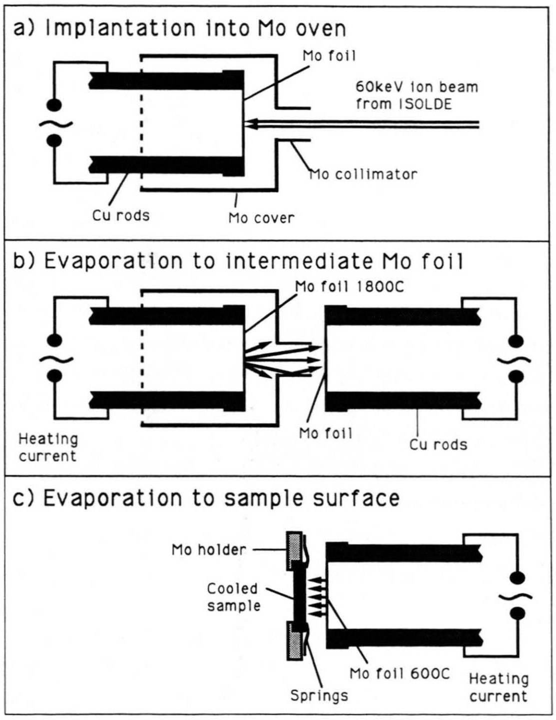

Fig. 3. Details of the two-stage deposition procedure.

The samples, mechanically and chemically polished, can be transferred from a 12 sample stack onto a low temperature measuring manipulator with a small handling manipulator. Surface cleaning is accomplished with the use of a sputter gun, electron beam heating, resistive heating, and a gas inlet system. Evaporation devices provide the option to deposit additional non-active materials to produce covered surfaces or thin films, the growth of which is controlled by the MEED [9] technique. The sample purity may be checked with a CMA Auger spectrometer. The chamber also contains a LEED analyzer for surface structure characterization. To eliminate vibrations that might impair future MS experiments, this setup can be full operated with non-moving pumps.

IIb) Off-Line Deposition

In special cases it has been possible to bring radioactive isotopes onto surfaces using conventional radiochemistry methods, properly adapted to the special requirements. Such procedures have been developed for the PAC cases ^{111}In [10] and ^{100}Pd [11]. Typically several chemical steps are needed for purification of the radioisotope. The subsequent evaporation onto surfaces follows the same principle as for on-line deposition.

IIc) Soft Landing

The scope of possible uses of nuclei for surface studies would be greatly enhanced if a direct deposition of the radioactive ion beam from the isotope separator on surfaces could be accomplished. With the high beam quality from ISOLDE this should in principle be possible [12]. The slowing down of the radioactive ion beam to a few eV has therefore been investigated theoretically. The blow-up of the beam spot size ac-

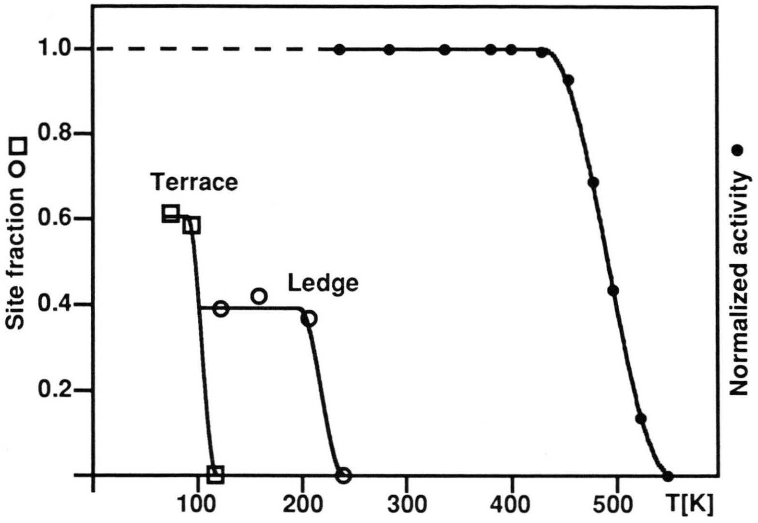

Fig. 4. Desorption isochrone measured for Cd from Mo(110) at heating times of 2 min, compared to surface site occupation found with PAC.

companying deceleration can be largely avoided if the retardation is performed in a very strong magnetic field that can coil up the ion path. Beam-optical calculations performed in collaboration with B. Moore, Montreal, have confirmed this idea. A deceleration system has been designed, making use of an available 10T magnet. The surface chamber ASPIC will allow to test this concept at the ISOLDE facility. To demonstrate that "soft landing" has occurred, one would deposit ^{111}In ions on a surface, e.g. Pd(111), where the efg signature of several surface sites is known from the PAC experiments described below.

IId) Thermal Desorption

The first thing one would like to find out to monitor the deposition process is if the probe atoms have actually been brought to the surface. With radioisotopes this is trivial, since one may simply measure the deposited activity. If one would also like to find out whether the atoms leave the surface again, one can measure the activity remaining on the surface after annealing in steps of increasing temperature and record the so-called desorption isochrones even for trace amounts. Such desorption isochrones have been recorded earlier with stable isotopes for many systems [13]. Due to the large coverage generally necessary, however, these curves are often quite complex and very difficult to interprete.

In the first experiments performed at ISOLDE the system Cd on Mo(110) was studied in detail [14]. We have demonstrated that the deposition of isolated radioactive ^{111m}Cd (48 min) atoms is possible. Figure 4 shows the simple thermal desorption isochrone observed for this system. It can be well described by desorption from a single (kink) site. Such experiments can only tell something about the nature of the final site from where the atoms are leaving the surface. Before they do so, however, they will have made many different diffusive displacements on the surface. The first project was therefore to investigate these motions by measuring the electric field gradients with the technique of perturbed angular correlation as described below. The interpretation of kink desorption is corroborated by the observation of well defined PAC spectra at lower temperatures.

Also the radioisotope ^{79}Rb (20 min) has been successfully used for such measurements on Mo(110).

III. Measurement Methods

Several nuclear methods are available to determine the quadrupole coupling in solids [15]. The splitting of the nuclear sublevels may be measured directly via high-resolution gamma spectroscopy (MS), as interference pattern in the time domain (PAC) or as temperature effect at very low temperatures (nuclear orientation). With polarized nuclei one can perform radiofrequency spectroscopy directly as in NMR/NQR, but monitored by nuclear counting. In all cases the nuclear radiation (mostly gamma or beta) is experimentally observed. Only the techniques applicable for surface studies shall be discussed here.

IIIa) PAC Experiments

Numerous descriptions of the perturbed angular correlation technique are available in the literature [16, 17, 18]. It makes use of a decay that emits a sequence of two gamma rays with an intermediate state halflife in the nanosecond time range. The orientation of the nuclear spin system is fixed by observing the first gamma ray in a detector. Since the emission of the second gamma ray is oriented relative to the nuclear spin, it will be anisotropic around this direction. For example the observation probability for γ_2 could be smaller at 90 degrees and larger at 180. If one then measures the coincidence count rate as function of time for detectors at 180° and 90°, the count rate would show the exponential decay of the nuclear level, but with a reduced counting rate at 90° due to this gamma anisotropy and an increased one at 180°. In the simplest case the ratio of the 180° to 90° degree count rates is then formed. Without perturbation it is

$$W(180)/W(90) = 1 + 3/2\, A_{22}$$

with A_{22} the nuclear anisotropy factor. If one applies a magnetic field perpendicular to the detector plane, the spin system will evolve in time. In the frame rotating with the Larmor frequency it will be stationary. Thus after a quarter of a Larmor period the detector at 90° will have a larger count rate and the one at 180° a small one. After half a Larmor period the original ratio is again found. Therefore the time spectra will be modulated with the frequency $2\bar{\omega}_L$. In general the ratio 180° to 90° will contain the information about the external perturbation acting on the nucleus.

For quadrupole precession basically the same description can be used. Due to the fact that here the nuclear sublevel splitting is not equidistant, however, the situation is somewhat more complicated. But again one can observe the interaction frequencies as a beat pattern in the count rate ratio.

A very suitable nuclear decay with an intermediate state of proper halflife and characteristics exists in ^{111}Cd as shown in Figure 5. Whereas generally the isotope ^{111}In is used as parent for PAC experiments, actually the 49 minute isomer also decays with suitable gamma rays through the shortlived $5/2^+$ level that is the probe state.

In the first on-line surface PAC experiment at ISOLDE radioactive $^{111\mathrm{m}}$Cd was brought onto a Mo(110) single crystal surface. Once the two-stage deposition technique had been developed, the expected perturbations for isolated adatoms were observed at 80 K [6]. At slightly higher temperatures the unique patterns disappeared, however, due to surface diffusion.

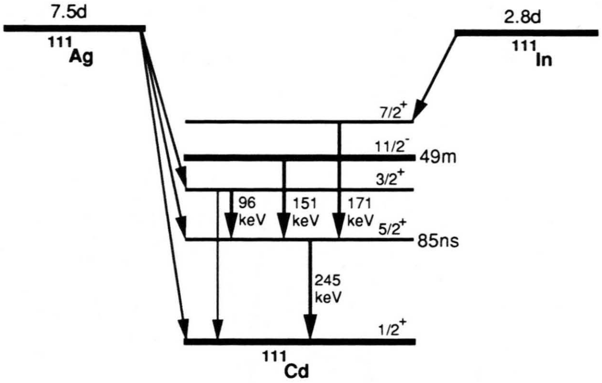

Fig. 5. Level scheme of the most popular PAC nucleus, ^{111}Cd.

On vicinal surfaces another pattern was observed at temperatures up to 250 K. Through the orientation dependence one can prove that indeed the atoms are sitting at the ledges. The PAC results for the case of cadmium at Mo(110) are included in Figure 4. After their initial landing at the terraces atoms on this rather close packed surface start to become mobile at very low temperatures, moving to the ledges. There they also become mobile at around 220 K, probably migrating to kinks from where they desorb.

A very simple model based on additive nearest-neighbor interactions (E_b) can account for the effects observed in this pilot system. An adatom at a close-packed surface is occupying a threefold coordinated site, leading to a binding energy of $3\,E_b$. In order to move from one of those sites to the other, one bond to neighbors has to be broken, leading to an activation energy for terrace diffusion of $1\,E_b$. The atom at a ledge site is bound to five nearest neighbors and for the motion along the ledge two of three bonds have to be broken, leading to a much higher activation energy for this motion. The deepest trap an adatom will find is the 6-fold coordinated kink site. The atom is bound to the kink with $6\,E_b$. From the combined PAC and desorption data one can estimate the activation energy for terrace and ledge diffusion as well as the desorption energy. One obtains 0.25 eV, 0.6 eV, and 1.5 eV, respectively, in good agreement with the predictions of the simple model. In Fig. 6 the potential energy for an adatom on a close-packed surface is shown schematically.

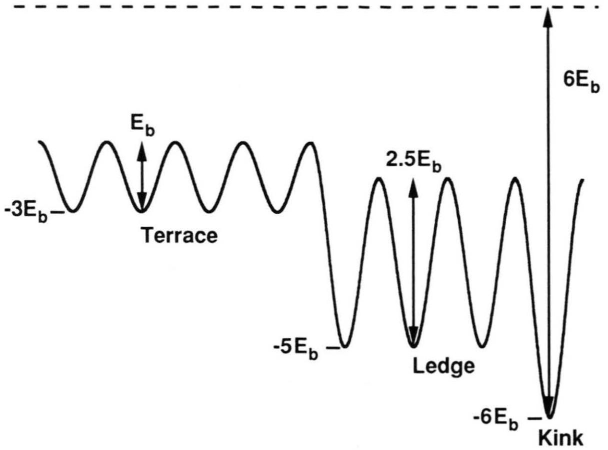

Fig. 6. Schematic potential energy of surface adatom in a nearest neighbor model.

Table 1. Further PAC Cases.

Source	PAC state	Remarks
^{111}Ag (7 d)	– ^{111}Cd (80 ns)	also beta-gamma
^{117}Cd (2.3 h)	– ^{117}In (120 ns)	
^{204m}Pb (60 m)	– ^{204}Pb (230 ns)	
^{100}Pd (4 d)	– ^{100}Rh (130 ns)	
^{79}Rb (20 m)	– ^{79}Kr (79 ns)	inert probe
^{77}Kr (48 m)	– ^{77}Br (9 ns)	
^{77}Br (56 h)	– ^{77}Se (9 ns)	
⋮		
^{19}O (29 s)	– ^{19}F (80 ns)	

In a further series of experiments at ISOLDE-2 the sites taken up by isolated In and Cd atoms on the model surface Pd(111) from the first landing position on the terraces up to their incorporation into the top surface layer have been characterized. The electric field gradient as observed with PAC was used as signature [19]. We have here not only used the isotope ^{111m}Cd to populate the perturbed angular correlation state, but also ^{111}In, which has slightly more favourable conditions for the measurements. In Fig. 7 typical PAC spectra measured on a vicinal surface for various annealing temperatures are shown. From the analysis of such data the characteristic interaction frequencies are found, and their contributions determined for the various annealing steps. As an example the results for a vicinal Pd(556) surface are represented in Figure 8. The symmetry of the efg as obtained from the interaction frequencies and the angular dependence of the PAC patterns is a strong help in assigning the observed components to specific surface sites. In Fig. 9 the identified sites for In and Cd on the Pd(111) surface are shown schematically. From the temperature dependence of their occupation the adatom diffusion for this system could be studied in detail [20].

From the first landing site on the terraces the atoms move to ledge sites. At higher temperatures they move to the kinks. The next sites taken up by the atoms are substitutional sites in the ledges, and finally substitutional sites in the terrace. This complete picture of surface diffusion for the Pd(111) system has clearly demonstrated the great potential of the nuclear techniques to investigate isolated impurities at surfaces and interfaces on a microscopic scale.

In a series of off-line experiments at Konstanz the isotope ^{111}In (2.7 d) has been deposited in a similar way. Monolayer coverages on In [21] as well as isolated impurities on several metallic surfaces [22, 23] could be studied by PAC. Also first results for a magnetic system, Cd on Ni [24, 25], have been obtained.

The PAC technique for surface studies has now reached a stage where the systems to be investigated may be selected due to their theoretical or technological relevance and not only their experimental feasibility. Out of the wide spectrum of possible applications, semiconductor surfaces and magnetic interfaces appear to be of particular interest.

Where are the future possibilities of such experiments? Obviously the experiments with ^{111}Cd using ^{111m}Cd and ^{111}In sources can be continued and many interesting new problems studied. A selection of further isotopes with suitable characteristics for PAC is presented in Table 1. For example one could use the same nuclear state in ^{111}Cd to also measure the sign of the electric field gradients using beta-gamma PAC [26], now with the ^{111}Ag parent. Several of the other very well suited isotopes are available from ISOLDE. For the studies of noble gases (^{79}Kr) [27], halogens (^{77}Br) [28] or chalkogens (^{77}Se) [29] the appropriate PAC isotopes have recently been used in solid state research. The potential is quite large and far from fully explored yet. Very recently the first PAC results using ^{100}Pd sources on surfaces were obtained [8].

IIIb) Mößbauer Spectroscopy

Another nuclear method that can be used to study the quadrupole splitting at surfaces is Mößbauer spectroscopy. It is a very powerful tool for obtaining microscopic information at the nucleus not only through

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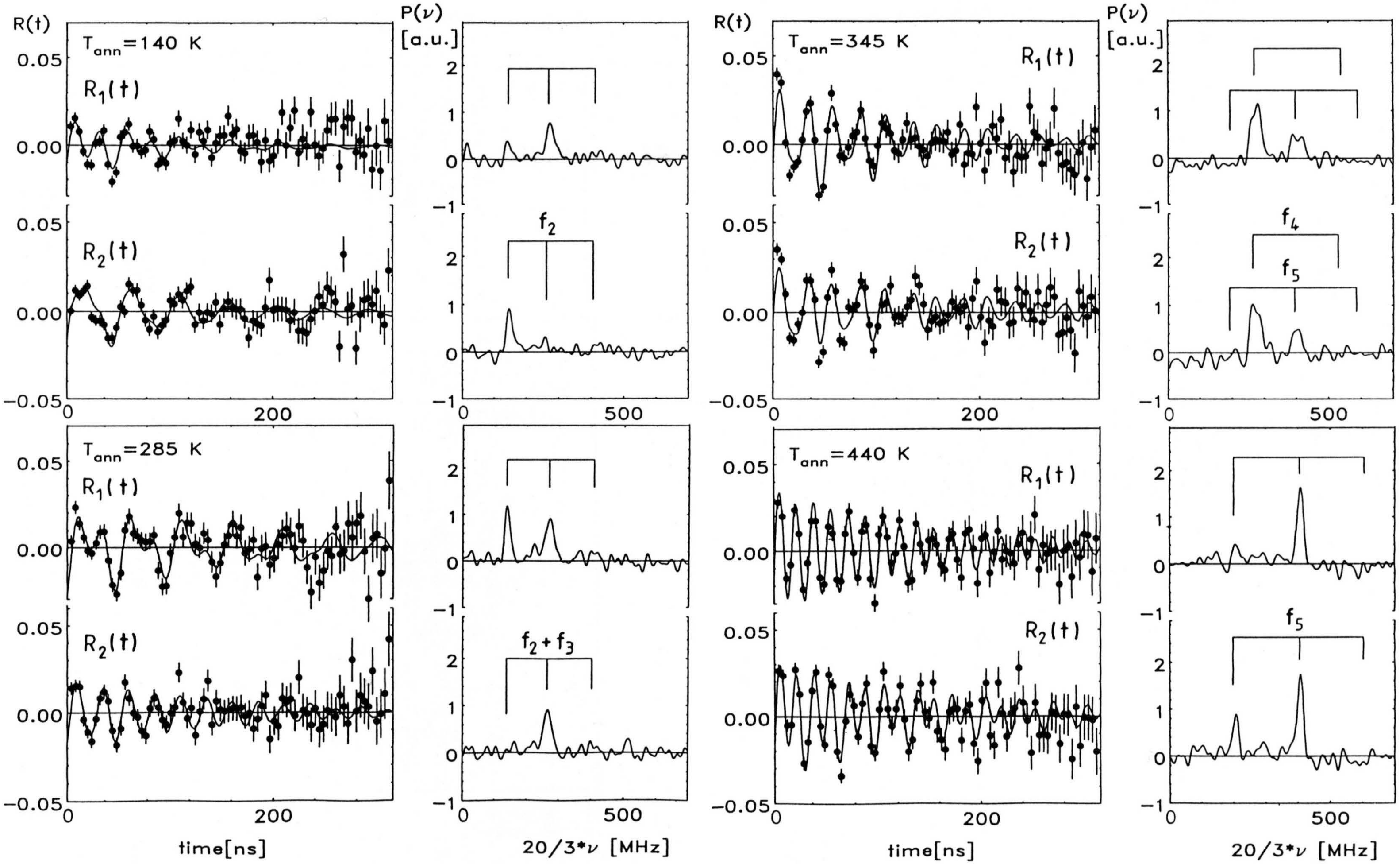

Fig. 7. Sample PAC spectra showing the dominance of different components on annealing.

hyperfine interaction (e.g. isomer shift, magnetic splitting, quadrupole coupling) but also through the Debye-Waller factor (DWF), that is particularly sensitive to the bonding environment. Such data for surfaces would be extremely valuable. An interesting prediction is that Mößbauer spectroscopy of adatoms at surfaces will show a very large anisotropy of the Debye-Waller factor. Rather hard phonons should exist perpendicular to the surface, while very soft ones are expected parallel to it.

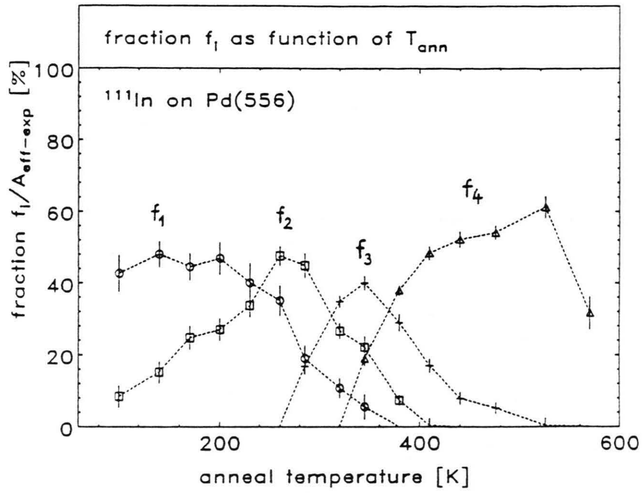

Fig. 8. Fraction of different components seen in PAC spectra as function of annealing temperature (f1–f4 correspond to the sites b–e in Figure 9).

Basically one could do source Mößbauer experiments with radioactive sources very similar to the PAC experiments. Up to now no data for isolated impurities exist, but there is a project at CERN with this goal. The strong sources obtainable at ISOLDE should make emission MS measurements feasible for several isotopes.

The ^{119}Sn $3/2^+$ Mößbauer state, very successfully applied to questions in solid state physics [30], is the optimal candidate. As it is produced in the decay chain from ^{119}Cd, the same sample preparation as for ^{111m}Cd PAC may be employed, resulting in completely complementary information. Very favorable conditions for ^{119}Sn MS are also found for ^{119}Sb sources that may be produced at ISOLDE in the decay chain of ^{119}Xe.

Iron MS measurements in absorption mode have been reported for a few surfaces at monolayer coverages [31, 32]. The conversion electron detection of Mößbauer spectra is sensitive enough for using a single monolayer of the isotope ^{57}Fe in Mößbauer spectroscopy.

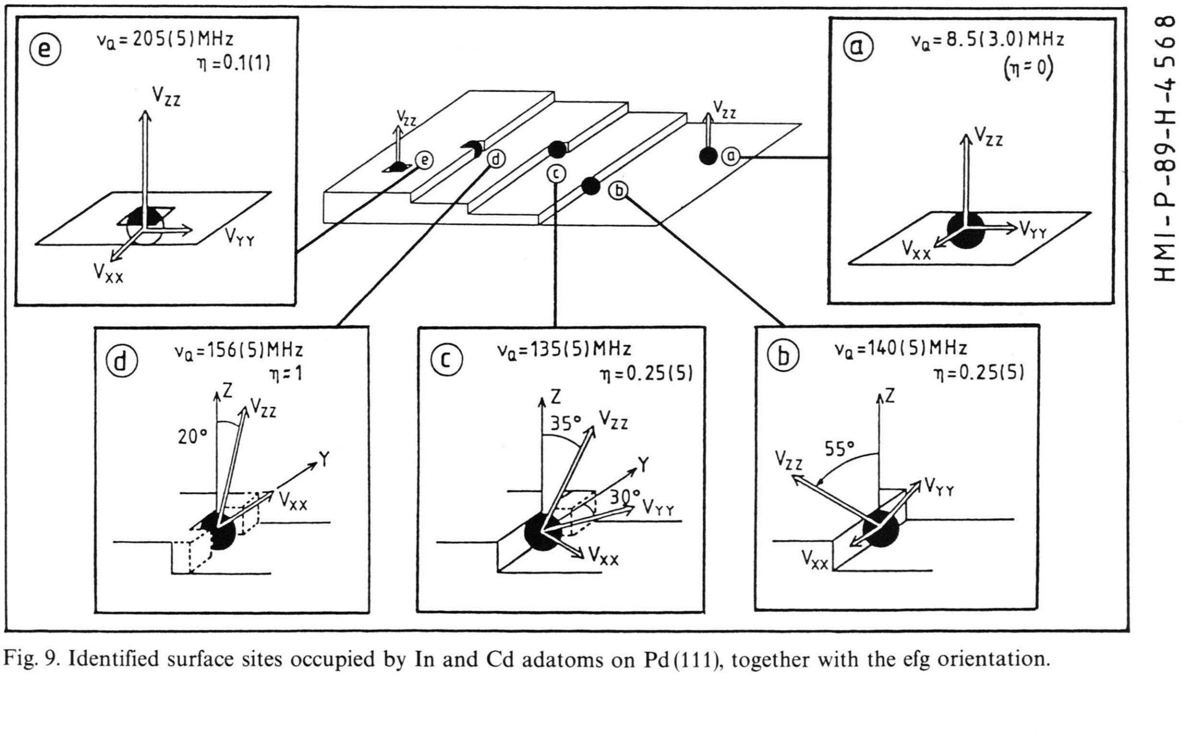

Fig. 9. Identified surface sites occupied by In and Cd adatoms on Pd(111), together with the efg orientation.

IIIc) Polarized Beam NMR

There is a third series of experiments that has produced information about field gradients for well defined surfaces, the polarized beam nuclear magnetic resonance studies by the group from Marburg [33, 34]. They are using a clever, basically nuclear counting technique [35], though the application is for stable isotopes. Highly polarized nuclear spins of alkali elements are produced, for example passing the atomic beam through a six-pole magnet, and these atoms deposited on surfaces. When the atoms are leaving the surface thermally again, their polarization can be investigated by severeal methods, one of them being laser spectroscopy. This implies, however, that the experiments in this form can only be performed at high temperatures. If one then applies a radiofrequency field while the atoms are resident on the surface, one can perform NMR on a very small number of atoms on the surface typically 10^{11}. Data for ^{6}Li, ^{7}Li and particularly ^{23}Na have been collected. Typical for the early data was that they have not been taken yet in very clean vacuum conditions. Therefore the metallic surfaces had to be cleaned regularly by flashing, and one observed changes of the efg as function of surface coverage, that is time after cleaning of the surface in the order of seconds.

Clearly the use of radioactive isotopes, where the nuclear polarization is detected by the anisotropy of beta emission, should be able to overcome the limitation of these experiments. In solids this β-NMR technique has been widely applied [36]. Such an experiment on surfaces is actually being attempted at Heidelberg with the isotope ^{8}Li [37]. Definitely the use of the intense ^{8}Li beam from ISOLDE would present a great advantage for such experiments. Also the use of the very efficient collinear laser polarization of ion beams available there [38] could be considered for surface applications.

IV. EFG Systematics at Surfaces

In addition to the PAC experiments with ^{111m}Cd and ^{111}In from ISOLDE used as examples here, the group at Konstanz has done similar experiments on a wide variety of metal surfaces using ^{111}In prepared in the laboratory as the PAC parent. The results are summarized in Table 2. The amount of information obtained is already rather impressive. For most surfaces more than one site could be characterized. Theo-

Table 2. Quadrupole coupling data for ^{111}Cd on metal surfaces.

Source	Solid	Surface	Site	e^2Qq/h [MHz]	eta	Ref.	Remarks
^{111}In	Ni	111	ST	228 (4)	0.05 (5)	[24]	
	Pd	111	ST	205 (3)	0.1 (1)	[19]	
			SL	156 (3)	0.95 (5)	[19]	
			K	135 (5)	0.25 (5)	[19]	
			L	140 (5)	0.25 (5)	[19]	
			T	8.5 (30)	(0	[19]	
	Cu	100	ST	181 (1)	0.05 (5)	[41]	$f(T)$
			SL	160 (2)	0.81 (2)	[41]	
			T	16 (1)	0.0 (1)	[41]	
		111	ST	202 (1)	0.05 (5)	[22]	In-In pairs
			SL	153 (1)	0.69 (1)	[22]	
			L	115 (1)	0.37 (2)	[22]	
		110	ST	159 (1)	0.74 (1)	[22]	Roughening
			ST2	98 (2)	0.50	[22]	
			ST3	16 (1)	(0	[22]	
			ST4	8 (1)	(0	[22]	
	Ag	100	ST	150 (1)	0.00 (5)	[23]	
			SL	125 (1)	1.00 (5)	[23]	
			L	113 (1)	0.12 (2)	[23]	
			T	6.5 (5)	0.00 (5)	[23]	
		111	ST	172 (1)	0.00 (5)	[50]	
			SL	145 (1)	0.83 (3)	[50]	
			K	155 (2)	0.35 (4)	[50]	
			S	119 (1)	0.21 (3)	[50]	
			Int	69 (1)	0.45 (5)	[51]	3 nm In
		110	ST	141 (1)	0.80 (1)	[50]	
	Au	100	ST	240 (5)	(0	[52]	
	In	111	ST	94 (3)	0.44 (4)	[53]	
^{111m}Cd	Mo	110	T	88 (5)	0.90 (3)	[6]	
			L	158 (6)	0.30 (3)	[6]	
	Pd	111	ST	196 (5)	0.05 (5)	[5]	
			SL	150 (6)	0.95 (5)	[5]	
			K	130 (5)	0.25 (5)	[5]	
			L	135 (5)	0.25 (5)	[5]	
	Cu	100	ST	180 (3)	0.05 (5)	[54]	

T = terrace adatom, L = ledge adatom; K = kink adatom; SL = substitutional ledge atom; ST (*n*) = substitutional terrace atom (in *n*th layer); Int = interface atom.

Table 3. Surface field gradients for various isotopes.

Isotope	Solid	Surface	Site	V_{zz} [V/Å]	eta	Ref.	Remarks
^{6}Li	Si	111	T	0.48 (2)	(0	[46]	
			Mon	0.90 (3)	(0	[46]	
^{7}Li	Mo	100		(+)0.30 (1)	(0	[45]	f(*T*, Oxygen, cov.)
		110		(+)0.54 (1)	(0	[45]	
	W	100		(+)0.65 (1)	(0	[45]	
		110	T	(−)0.11 (1)	(0	[33]	
^{23}Na	W	100	T	(−)0.9 (1)	(0	[45]	
		110	T	(−)5.6 (1)	0.07 (1)	[45]	
		112	T	(+)4.0 (5)	0.7 (2)	[34]	efg in plane
^{57}Fe	Fe	110	ST	(+)87 (20)		[48]	
			ST2	(−)15 (10)		[48]	
			Int	(+)66 (15)		[48]	Ag covered
	W	110	Mon	(+)80 (15)		[32]	Fe monolayer
			Int	10 (10)		[32]	We-Fe-Ag Sandw.
^{100}Rh	Pd	111	ST	71 (2)	(0	[8]	Pd source
^{111}Cd	Si	100	2 × 2	185 (15)	0.23 (3)	[42]	Reconstruction
			4 × 3	247 (32)	0.25 (5)	[42]	
			Bulk	34 (4)	0.0 (1)	[44]	Local distortion

Abbreviations as in Table 2; Mon = monolayer; $n \times n$ = surface reconstruction.

retical calculations using a molecular cluster model appear to be in qualitative agreement with the experiments [39]. Also some measurements of the temperature dependence of the efg have been made. Only two very characteristic features shall be pointed out here:

1) For Cu(110) the effect of covering the deposited radioactive isotopes with further copper has been investigated [40]. In this way substitutional atoms in the third and fourth layer could be created. Rather small quadrupole interaction constants were measured, demonstrating that a nearest-neighbor description of the electric field gradient is quite appropriate. Both the third and fourth layer have already the twelvefold coordination of bulk Cu, leading to an effectively cubic environment as indicated by the small field gradients.

2) Only in a few cases have field gradients for Cd atoms sitting on terraces of fcc metals been measured (Cu(100) [41], Pd(111) [19] and Ag(100) [23]). The values found are unexpectedly small. A nearest-neighbor model, however, would predict very large ones, at least of the order of the vacancy field gradients. A qualitative interpretation of this discrepancy can be found in the tight-binding model proposed for explaining field gradients in sp-metals [14]: For the cadmium atom the electronic structure is rather peculiar because the free atom has a $5s^2$ configuration and no p-electrons. To create asymmetric p-orbital occupation one has first to populate the 5p band and then to broaden it asymmetrically. The population is made by all the nearest neighbors, so the higher the coordination is, the more p-electrons are available to be then polarized by the asymmetry of the surrounding. Cadmium, if it is not highly coordinated, behaves like an s-electron atom. This can very easily account for the qualitative observation, since the terrace adatom sites have a small coordination number.

The surface efg data obtained for systems other than ^{111}Cd on metals are summarized in Table 3. For better comparison, they are all given in V/Å^2, a natural unit for atomic energies and dimensions.

First data for ^{111}Cd on semiconductor surfaces have been obtained by the Konstanz group [42]. Such surfaces are very rich in possible structures and therefore have to be prepared with great care. A comparison of the experimental values with theoretical ones is hampered by the fact that the calculations [43] have been done for non-reconstructed surfaces. At least a qualitative agreement can be noted, however. For silicon the influence of the surface on the field gradients at Cd impurities in the bulk has been observed to be of very large range [44].

Very recently the first results have been obtained for a further PAC nucleus, ^{100}Rh, using ^{100}Pd sources [8]. The electric field gradient for Rh incorporated in a Pd(111) surface was measured. It is actually of the same order of magnitude as the ones found for the Cd probes nucleus.

In addition to the early measurements for lithium and sodium on tungsten surfaces [33, 34] mentioned above, where field gradients and their signs have been determined by polarized beam NMR, there are some similar recent experiments performed with ^{7}Li on Mo and W surfaces [45] as well as first data for Si(111) [46]. The surface efg on metallic systems has also been treated theoretically within a jellium model [47].

The field gradient at the surface atoms on Fe(110) could be measured and a value of $+87$ V/Å^2 has been determined [48]. Also theoretical calculations for this system have been reported, in good agreement [49]. Very interesting here is that already in the second layer the field gradient is found to be unmeasurably small. Covering the surface with Ag, however, does not very much reduce the efg. This is in contrast to the Fe monolayer on W(110), where the large efg is completely quenched by Ag coverage [32].

V. Conclusions

It is by now quite clear that the use of PAC, Mößbauer spectroscopy and Beta-NMR for surface studies with radioactive sources will grow substantially in the near future and yield a wealth of microscopic information about such systems, particularly through the nuclear quadrupole interaction. The most important bottleneck is the small number of radioisotopes accessible for such measurements at present. The wide range of isotopes available at a modern radioactive ion beam facility like ISOLDE, however, offers enormous potential in this respect. The development of a "soft landing" technique would be a great step forward in its exploitation.

One could think of several other hyperfine interaction techniques using radioisotopes for surface studies, e.g. low temperature nuclear orientation, though the associated technical problems would be formidable. The full potential of the nuclear methods will certainly be most important in the study of interfaces, where virtually no competing classical methods exist.

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