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Sensitive Probing of Surfaces by Electric Quadrupole Interaction Demonstrated for Indium Metal

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(Received 6 October 1982)

The electric quadrupole hyperfine interaction at indium surfaces has been detected with use of the perturbed angular correlation technique. The electric-field gradient at the surface is found to be $|V_{zz}$ (surface)|= $5.6(6) \times 10^{17}$ V/cm² with an orientation perpendicular to the surface. This is a drastic enhancement of the field gradient compared with bulk by a factor $|V_{zz}$ (surface)/ V_{zz} (bulk)| ≈ 4 . The result is discussed in a simple one-Wigner-Seitz-cell model.

PACS numbers: 71.70.Jp, 73.90.+f, 76.80.+y

The behavior of electromagnetic properties near and at surfaces and interfaces is of great interest for the understanding of interactions between atoms under these boundary conditions. Hyperfine methods, such as nuclear magnetic resonance (NMR), Mössbauer effect (ME), and perturbed angular correlation (PAC), offer high sensitivity at interatomic ranges for the study of electromagnetic fields present in these quasitwo-dimensional systems. Magnetic hyperfine fields at surfaces are of special importance for the understanding of exchange interactions; electric hyperfine fields are quantities sensitive to structural and electronic variations near the surface.

ME studies, performed exclusively with ⁵⁷Fe, have established deviations of the magnetic hyperfine field at interfaces from the bulk value.¹⁻³ NMR investigations of chemical shifts at surfaces have demonstrated their importance for adsorption processes.⁴ On the other hand, information on electric hyperfine fields is only fragmentary. Electric-field gradients for isolated atoms on glass,⁵ tungsten, and silver⁶ substrates have been noticed in ⁵⁷Fe ME work but have not been further pursued.

In this Letter we report the first detailed study of the electric-field-gradient (efg) tensor at the surface of indium metal utilizing the PAC method. This method allows measurement of the efg via the quadrupole hyperfine interaction of radioactive probe atoms located near and at the surface. Therefore the efg can serve as a signature of atoms on the surface, which can be employed for further surface and interface studies.

As a system we have chosen indium (tetragonal structure) doped with ¹¹¹In probes to reduce complications from chemical impurity effects and to achieve best growth conditions. A sample typically consisted of a 400-Å-thick film of natural indium, which was evaporated onto a glass backing at 100 K and was annealed at 200 K. Annealing was controlled by resistivity measurements. This procedure should create In substrates with textures where the [111] direction is preferentially oriented perpendicular to the surface.⁷ Depositions of various thicknesses (3-50 Å) were then added onto the cooled substrate (T = 100 K); first In doped with radioactive ¹¹¹In (typical concentration 10^{-5}) was evaporated from a second oven and then inactive In was deposited. The thickness was monitored with a quartz oscillator system to an accuracy of about 1 Å at 3 Å thickness. In order to reduce γ background from the residual activity in the second oven, the cooled sample was transferred from the evaporation region to a shielded detection position without breaking the vacuum. This allowed positioning of four γ detectors outside the vacuum in the sample surface plane to measure the PAC spectra. The samples

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were prepared and kept for all experiments in ultrahigh vacuum ($\approx 10^{-10}$ Torr): altogether three In samples with various depositions were investigated.

The PAC technique makes use of the isomeric nuclear state $(I = \frac{5}{2}, T_{1/2} = 84 \text{ ns})$ intermediate between the 172-247-keV γ - γ cascade in ¹¹¹Cd which is populated through the ¹¹¹In decay $(T_{1/2} = 2.8 \text{ d})$. The nuclear quadrupole moment of this state (Q = +0.80 b) senses the efg produced by the extranuclear charges. PAC time spectra were recorded with a conventional four-NaI-detector setup and were analyzed by evaluating the usual counting-rate ratio R(t).⁸ The presence of a nonvanishing efg acting on the probes is expressed in the R(t) spectrum as a superposition of three frequencies,

$$R(t) = 1 + \sum_{n=0}^{3} a_n \cos(c_n \omega_0 t) \quad (c_0 = 0), \tag{1}$$

with the interaction frequency⁹ $\omega_0 = 3e Q V_{zz}/20\hbar$, where V_{zz} is the largest component of the efg tensor in the principal-axis system. The coefficients a_n depend on nuclear properties; they reflect the orientation of the principal-axis system with respect to the detector plane, they show whether the axis system is uniquely or statistically oriented within the sample, and finally they contain, together with the parameters c_n , information on the symmetry of the efg tensor (for details see Ref. 10). In the case that more than one efg, with fractions f_i , are acting on the nuclear probes, R(t) has to be expanded,

$$R(t) = 1 + \sum_{i} f_{i} \left\{ \sum_{n=0}^{3} a_{n}(i) \cos[c_{n}(i)\omega_{0}(i)t] \right\}.$$
 (2)

In Fig. 1, two selected PAC time spectra together with the corresponding Fourier transformations are displayed, exhibiting the surface effects most clearly. The least-squares fits to the PAC time spectra (solid lines) are based on Eq. (2) including an additional Lorentzian frequency distribution. The upper spectrum [Fig. 1(a)] was obtained from ¹¹¹In probes distributed in a 3-Åthick deposition [corresponding on the average to 1 monolayer: d(111) = 2.7 Å on top of the In substrate. The probes recognize two different efg: About 48% are exposed to the well-known In bulk efg¹¹ ($|\omega_0| = 24$ Mrad/s), with the three frequencies broadened as expected for thin In films¹²; another fraction of 52% senses a much larger efg corresponding to $|\omega_0| = 102$ Mrad/s with the remarkable feature that only one frequency is prominent. This new efg is associated with In probes



FIG. 1. PAC time spectra (left) with their Fouier transformations (right) for two different In depositions: (a) $In^{111}In/(In substrate) = (3 \text{ Å})/(400 \text{ Å})$; (b) $In/In^{111}In/(In substrate) = (2 \text{ Å})/(3 \text{ Å})/(400 \text{ Å})$. The solid lines in the PAC spectra represent least-squares fits based on Eq. (2); fit parameters for the frequencies and their weights (arbitrary units) are indicated as bars under the Fourier spectra.

at the surface as our further experiments show.

The lower spectrum, Fig. 1(b), was taken from the same sample with an additional 2-Å inactive-In deposition. The same two efg are observed, however with considerably changed fractions (see also the Fourier spectra): f(bulk) = 77% and f(surface) = 23%. This demonstrates that ¹¹¹In atoms which first probed the surface efg are now probing a larger fraction of the bulk efg because of the additional deposition. An illustration of this situation is shown in Fig. 2.

We can summarize all our results as follows:

(i) In all cases, only the bulk efg $[|\omega_0| = 24(1)$ Mrad/s with $\Delta \omega_0/\omega_0 = 15\%$] and a second efg, characterized by $|\omega_0| = 102(3)$ Mrad/s (with $\Delta \omega_0/\omega_0 = 7\%$) and a value of $|V_{zz}| = 5.6(6) \times 10^{17}$ V/cm², are observed within statistical significance. From its behavior as a function of additional inactive depositions this new efg is attributed to probes at the surface. The two well-separated frequencies imply that the efg is governed by the charge distribution within an atomic distance; otherwise, intermediate efg values should occur.

(ii) The coefficients a_n for the bulk efg $|a_1| = 0.015(2)$, $a_2 = 0.036(2)$, $a_3 = 0.017(2)$] are consistent with the V_{zz} axis oriented at $\theta = 33^\circ$ with respect to the surface plane. This is consistent with the In substrate growing preferentially with a (111) surface.

(iii) From the fact that only one frequency for the surface efg is visible we conclude that this efg has axial symmetry (or is very close to it) and is oriented perpendicular to the surface (i.e., $a_2 = a_3 = 0$, $c_1 = 1$, $c_2 = 2$, $c_3 = 3$).



FIG. 2. Illustration of the fractions of bulk efg (dotted area) and surface efg (black area) probed by ¹¹¹In atoms for various depositions on indium: (a) active deposition of 1 monolayer on the average; (b) additional inactive deposition of 1 monolayer on the average; (c) additional inactive deposition of 2 monolayers on the average.

(iv) Successive monolayer growth for In on the In substrate can be excluded since a $3-\text{\AA}$ active deposition [see Fig. 1(a)] results already in two efg with about equal fractions. Figure 3 shows the change of the two efg fractions as a function of additional inactive depositions. From this we can estimate an average roughness of deposited In on the In substrate to be of the order of 3 monolayers.

In order to understand better the properties of the observed surface efg we have made a theoretical estimate. Traditionally the efg at a nuclear site is separated into contributions due to discrete ion charges and conduction electrons, both modified by appropriate Sternheimer factors.¹³ Bodenstedt and Perscheid¹⁴ have approximated the generally complex conduction-electron distribution by point charges centered at the faces of the Wigner-Seitz polyhedra. This rather simple model seems to reflect the essential features of the efg in metals. Therefore we have calculated the efg within this picture following the zero-order approximation which expresses the fact that the efg at an ionic site is predominantly produced by the conduction electrons in the one neutral Wigner-Seitz cell. Consequently the range of the efg in this approximation is just an atomic distance, which is supported by our results. For In bulk we have adjusted the effective ion charge Z_{eff} and charge shift δ so that the experimental value $[V_{zz}^{exp} = -2.18(3) \times 10^{17} \text{ V/cm}^2 \text{ (Ref. 11) for } In^{115} \text{In}$ (Ref. 15) is best reproduced by theory and above all, agrees in sign:

$$V_{zz}^{\text{theor}} = -0.8 \times 10^{17} \text{ V/cm}^2$$

(for Z_{zz} = 3 $\delta \simeq 0$).



FIG. 3. Change of the fractions for bulk efg and surface efg as a function of additional inactive-In deposition onto a sample with $In^{111}In/(In \text{ substrate}) = (3 \text{ Å})/(400 \text{ Å})$.

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A (111) cut through the Wigner-Seitz cell and a rearrangement of the electronic charges situated above that cut can now model the situation for the surface efg. Geometric reconstruction of the surface atoms caused by the electronic redistribution should also be considered in principle. However, for (111) fcc surfaces the atomic structure is distorted only by a few percent,¹⁶ which suggests that atomic reconstruction can be neglected for our estimate. For the most extreme electronic redistribution, i.e., all the electronic charges above the (111) plane are equally distributed in the plane, we find (with $Z_{\rm eff}$ and δ from bulk) an almost perfect axially symmetric efg with $V_{zz}^{\text{theor}} = +16 \times 10^{17} \text{ V/cm}^2$ oriented perpendicular to the (111) surface. This result, namely perpendicular orientation and enhanced efg $\left[|V_{zz}^{\text{theor}}(\text{surface})/V_{zz}^{\text{theor}}(\text{bulk})| = 20 \right]$ at the surface, persists qualitatively for other possible electronic redistributions as well and is in agreement with our results.

Our experiments have demonstrated that a well defined efg which is much larger than the bulk value $[|V_{zz}|^{\exp}(\operatorname{surface})/V_{zz}|^{\exp}(\operatorname{bulk})| \approx 4]$ is present at the surface of In metal. This surface efg can be explained by a modified conduction-electron distribution at the surface. In general such surface field gradients should be created by the electronic and atomic redistributions as a reaction to the symmetry distortion at the surface and therefore should be a common feature for metal surfaces.

The range of the efg in a metal is shown experimentally to be of the order of an interatomic distance, which makes the efg a very sensitive quantity to changes of the electronic and the atomic distributions at the surface. Conceivable applications arise from the possibility to prepare films with efg-marked surface atoms in studies of growth and adsorption of atoms at surfaces, of intermetallic alloys at metal-metal interfaces, and of diffusion of surface or interface atoms.

The authors are grateful to Dr. P. Heubes, Professor E. Recknagel, and Dr. A. Weidinger for stimulating discussions. This work was supported by the Deutsche Forschungsgemeinschaft.

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