estimated from their measured resistivities by assuming a hole mobility of 300 cm^2/V sec. For the SI and n-type samples, an electron mobility of 4000 cm^2/V sec was assumed. These mobility estimates are not critical to the conclusions reached below.

The calculated Cr^{4+}, Cr^{3+}, and Cr^{2+} concentrations are presented along with the measured (EPR) concentrations in Table II. The agreement is quite remarkable, considering the various possible sources of error, and leaves no doubt that the measured electrical activation energy indeed corresponds to the Cr$^{4+}\to$Cr^{3+} transition. Note that the difference in temperature between the EPR measurements (4.2 K) and the electrical measurements (295 K) is unimportant here, because, in both cases, $p \ll |N_{DS} - N_{AS}|$, and thus, from Eq. (4), the $N_{\mathrm{Cr}^{4+}}$ concentration should remain nearly the same from 4.2 to 295 K.

In summary, we have, for the first time, conclusively identified a transition which involves Cr^{4+} in GaAs namely the Cr$^{4+}\to$Cr^{3+} thermal transition. Room-temperature thermal energies, with respect to the valence band, can now be given for all three transitions: $E_1(4+\to 3+) = 0.28 \pm 0.01$ eV; $E_2(3+\to 2+) = 0.74 \pm 0.02$ eV; and $E_3(2+\to 1+) = 1.54 \pm 0.01$ eV. By assuming that the recent photo-EPR[2,3] and photoconductivity[7,8] results pertain to the *optical* (absorption) Cr$^{4+}\to$Cr^{3+} transition, we can deduce a Franck-Condon shift of about 0.12 eV, at 150 K.[7]

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He-Scattering Investigation of CO Migration on Pt(111)

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The capability of a He-scattering experiment to detect the migration of adsorbed molecules on monocrystal surfaces is demonstrated for the first time. CO migration and island formation can be investigated at very low coverages because of the very large cross section for He scattering of CO adsorbed on Pt(111). The activation energy for CO migration on Pt(111) is found to be 7 kcal/mole. No island formation at low CO coverages on a defect-free Pt(111) surface was detected in the temperature range 120-400 K.

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A few years ago Schmidt stated that "measurements of surface diffusion rates on single-crystal planes are exceedingly difficult."[1] Reed and Ehrlich noted in a recent paper[2] that, except for a number of field-emitter studies, the migration of adsorbed gases on single-crystal surfaces has been investigated only in a couple of cases: O (Ref. 3) and N (Ref. 4) on W(110). In addition, the methods used so far apply at coverages at which interactions between adsorbates are likely to be strong and thus to interfere in the migration process. It is the purpose of this report to show that because of the particular features of thermal He scattering the measurement of surface diffusion may become a straightforward procedure. Moreover, the very large scattering cross sections of adsorbed gases for incident He beams [$250\ \text{Å}^2 < \Sigma < 550\ \text{Å}^2$ for CO on Pt(111)[5]] make it possible to investigate the migration of adsorbed gases in its genuine form at very low coverages and also to study the island formation.

The principle of the measurement of adsorbed-molecule migration on low-index crystal surfaces proposed here is as follows. A given amount of molecules are adsorbed onto the crystal surface at a temperature low enough to ensure that the adsorbed molecules stay immobile. During subsequent (linear) heating the coverage on the low-index face varies because of the migration to (or from) defect sites (steps/kinks) as soon as the adsorbate mobility sets in. The migration direction is determined by the free-energy difference between molecules adsorbed at low-index and defect sites and by the initial coverage on the two kinds of sites (i.e., by the respective sticking probabilities). The coverage on the low-index sites is monitored by measuring the intensity of the specular He beam, which is a good measure of the coverage on defect-free areas, at least for low coverages and disordered adsorbates.[6,7]

The feasibility of the above procedure is based on the unique capability of the molecular-beam scattering to discriminate directly between properties of low-index and defect sites.[6-8] This is due to a negligible contribution of the He scattering around defect sites to the coherent specular beam, when compared with the contribution of the low-index areas.[7,8] Accordingly, a reduction of the coverage on the low-index sites due to adsorbate migration will result in an important increase of the specular He-beam intensity.

The measurements reported here were performed with a highly collimated He nozzle beam of 63 meV in a system described previously,[6,8] at a small angle of incidence (40°).[8] The Pt(111) crystal surface was prepared with an improved aligning and polishing technique,[9] resulting in a high reflectivity due to a defect concentration of less than 10^{-3} step and kink sites.[7,8] This surface is called an "ideal" Pt(111) surface. Defects were induced when necessary by bombarding the surface with $(0.5-1)\times 10^{14}$ Ar ions/cm^2 (600 eV). A very rough estimation of the defect concentration after bombardment and coalescence of the individual vacancies at room temperature gives a few times 10^{13} step atoms/cm^2 and a few times 10^{12} kink atoms/cm^2 concentrated in $10^{11}-10^{12}$ pits/cm^2.[10] The reflectivity for He scattering of the bombarded surface is about 20% of the reflectivity of the "ideal" Pt(111) surface.

Figure 1 shows the decrease of the He specular-beam intensity as a function of CO exposure at constant pressure ($p_{\text{CO}} \simeq 3\times 10^{-9}$ mbar) and constant temperature. The semilogarithmic adsorption plot obtained with the "ideal" Pt(111) surface (crosses) at room temperature shows a perfect linear behavior over more than two orders of magnitude. The slope of the line corresponds to the scattering cross section of adsorbed CO for 63-meV incident He of $\Sigma = (265/s_0)$ Å^2 where s_0 is the sticking probability[5] [$s_0 \approx 0.84$ (Ref. 11)]. The adsorption isotherm taken with the same surface at $T = 120$ K is identical within the experimental errors with the room-temperature curve, but not shown.

In contrast, the adsorption plot obtained at room temperature with the bombarded surface

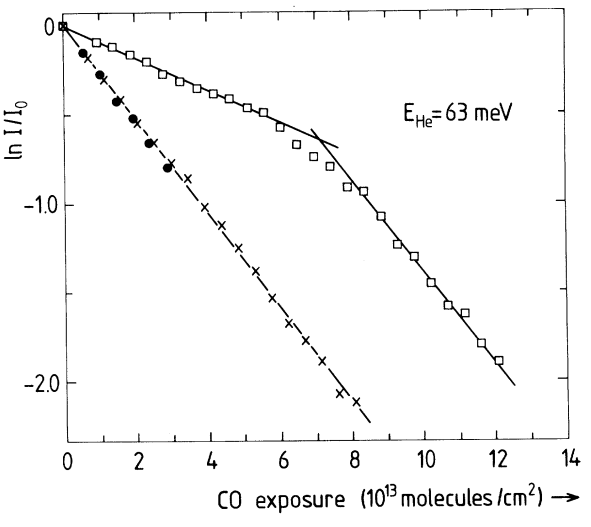

FIG. 1. He specular-beam intensity, I, vs CO exposure at constant pressure ($p_{\text{CO}} \simeq 3\times 10^{-9}$ mbar) and constant temperature. The He beam is scattered from an "ideal" Pt(111) surface at 293 K (crosses) and from a Pt(111) surface with defects at 293 K (open squares) and 107 K (filled circles). I_0 is the He intensity from the corresponding clean surface at the temperature of the respective adsorption experiment.

(open squares) shows a completely different, "two phase" behavior. A similar behavior was observed with a kinked (12 11 9) Pt surface at room temperature[8] and was interpreted as follows: During the first phase the CO adsorbed on (111) terraces migrates to the defects (especially to the kinks) where it is more strongly bound. Accordingly, the rate of decrease of the specular He intensity is lowered. The resulting higher effective coverage at the defect sites has only a marginal effect. This explanation holds equally well for the present case. When the defect sites start to saturate (at an exposure of about 7×10^{13} molecules/cm^2 in Fig. 1) the migration ceases and the behavior in the second phase parallels the adsorption on the "ideal" Pt(111) surface. This interpretation is supported here by two additional observations: (1) The exposure at which saturation occurs depends as expected on the amount of defects, i.e., on the Ar$^+$ dose, and (2) the adsorption plot at $T=107$ K obtained with the bombarded surface (filled circles) is *identical* within the experimental errors with the adsorption plots obtained with the "ideal" Pt(111) surface. This demonstrates that the intensity of the He beam is indeed a good measure for the coverage on undisturbed (111) areas of the bombarded surface, which is identical to the coverage on the "ideal" Pt(111) surface as long as the CO molecules remain immobile after adsorption.

It is now obvious that by stopping the $T=107$ K exposure on the surface with defects at a certain value (as shown in Fig. 1) and then heating the sample, the specular He-beam intensity will start to increase as soon as the adsorbed molecules become mobile and migrate to the defects. The He intensity will eventually reach the corresponding value on the "two-phase" curve. This direct evidence for the migration process is shown in Fig. 2, where $\ln(I/I_0)_{\rm DW}$ is plotted as a function of temperature. I_0 is the intensity of the He specular beam from the clean surface at the lowest temperature. The data are corrected for Debye-Waller effects (index DW) by use of a Debye temperature of 230.6 K. This temperature was deduced from a $\ln I/I_0$ versus T plot measured on the clean "ideal" Pt(111) surface which was perfectly linear in the whole temperature range 100–500 K. (A value of 231 K was obtained from the same surface through a plot of I/I_0 versus Δk.[7])

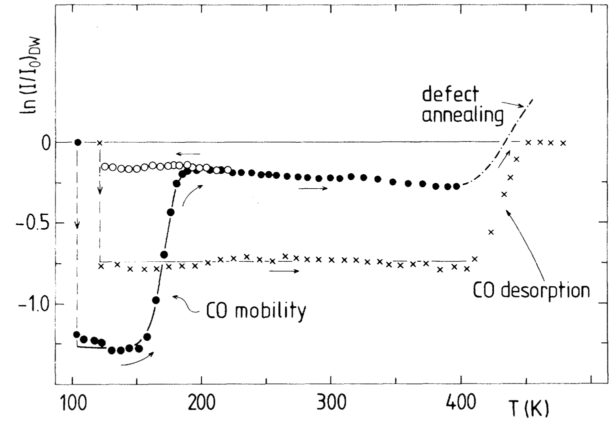

FIG. 2. Relative He specular-beam intensity (I/I_0) vs surface temperature. The He beam is scattered from a Pt(111) surface with defects (filled circles for heating and empty circles for cooling) and from an "ideal" Pt(111) surface (crosses) which were initially CO covered at low temperatures (coverage 2.5% and 1.5%, respectively). I_0 is the He intensity scattered from the corresponding clean surface. The ratio of the I_0 values for the "ideal" surface and the surface with defects is about 5. The data are corrected for Debye-Waller effects (see text).

The adsorption at constant temperature on the surface with defects (filled circles) preceding the heating procedure is shown in Fig. 2 as a vertical dashed line at $T=107$ K reaching a final value $\ln(I/I_0)_{\rm DW}=-1.20$ corresponding to a coverage of about 2.5% on the defect-free areas. The sample is now heated almost linearly ($\beta\simeq0.4$ K/s). The He intensity first stays almost constant and then above 150 K increases dramatically up to $\ln(I/I_0)_{\rm DW}=-0.17$ at about 190 K. This curve segment reflects the decrease of the CO coverage on defect-free areas due to the CO migration to defect sites. The probability in unit time for a CO molecule to reach a defect site is equal to the density of defects times the hopping frequency $\nu\exp(-Q/RT)$. By insertion of $T=T_0+\beta t$ the best fit, represented by the solid line, was obtained for $Q=7$ kcal/mole. For the preexponential factor a value of $10^{11}-10^{12}$ s^{-1} is found, if the defect densities given above are used. This value of the activation energy is in fair agreement with the general statement of Schmidt[1] (10% – 20% of the binding energy) but significantly smaller than the sole (field emission) value obtained yet for the system CO/Pt under quite different conditions.[12]

If the heating is continued beyond the point where the migration to the defect sites is completed, the He intensity slightly decreases (see below) up to 400 K. Above this temperature the He intensity strongly increases (dot-dashed line), surpassing eventually its "clean state" value. This increase in reflectivity is due to the annealing of the defects produced at room temperature. This was confirmed in a separate experiment by heating a clean bombarded surface. The behavior above 400 K was similar and the He intensity reached eventually the "ideal" Pt(111) value.

If, instead of annealing the defects, the temperature run is reversed anywhere between 190 and 380 K, the He-intensity data (open circles) taken during the cooling down to about 190 K reproduce the data measured during heating up (filled circles). Beyond this point the intensity remains fairly constant down to the lowest temperature. A renewed heating reproduces the cooling data. This behavior is consistent with the picture gained so far.

A similar run consisting of adsorption at $T = 120$ K up to a certain coverage $[\ln(I/I_0)_{\mathrm{DW}} = -0.75 \rightarrow \theta_{\mathrm{CO}} \simeq 1.5\%]$ followed by an almost linear heating ($\beta \simeq 0.83$ K/s), but performed on the "ideal" Pt(111) surface, is also shown (crosses) in Fig. 2. The Debye-Waller–corrected He intensity is constant throughout the whole temperature range up to 400 K. Above this point the CO starts to desorb and accordingly the He intensity increases, reaching eventually at about 460 K the clean "ideal" Pt(111) value when all CO is gone. This last segment is in fact an integral temperature-programmed desorption (TPD) curve. In the usual differential form the curve peaks around $T_p = 435$ K. The peak temperature for a heating rate $\beta = 15$ K/s can be calculated from Fig. 2 by assuming first-order desorption. The resulting $T_p \simeq 480$ K is in fair agreement with TPD peak temperatures obtained from defect-free Pt(111) surfaces, where T_p tends to values between 485 and 495 K for very low CO coverages.[13-15]

The absence of a He intensity increase when the CO molecules adsorbed on the "ideal" Pt(111) surface become mobile leads to two conclusions:

(1) The defect density on this surface is extremely low, in accordance with previous structure determinations.[7] Indeed, the relative coverage decrease due to CO migration to defect sites is not detectable in spite of the very low total coverage (~ 1.5%). In the future, this kind of experiments and argumentation may become a very sensitive method for the quantitative titration of defects.

(2) On a defect-free Pt(111) surface and at low coverages there is no CO island formation in the temperature range 120–400 K. Indeed, the diameter corresponding to the huge scattering cross section of an adsorbed CO molecule $[d \simeq (18.4/\sqrt{s_0})$ Å$]$ is much larger than any reasonable mutual distance between neighboring CO molecules belonging to an island. Accordingly, if the adsorbed CO molecules, after becoming mobile, gather to islands, a dramatic increase of the He intensity should be observed. This seems to be a most straightforward method to watch the formation and the gradual dissolution of islands with temperature, at least on defect-free surfaces. In the presence of defects, in particular when the nature and the number of defects is only roughly known, it is hardly possible to distinguish between adsorption of individual CO molecules at defect sites and the formation of CO islands with a defect site as nucleation center. The already mentioned slight He-intensity decrease between 190 and 400 K might, in principle, be interpreted as an increase of the CO coverage on defect-free areas due to the detachment of CO molecules from defect sites or to a decrease of the island size. Experiments with better defined defects are in progress.

Conclusions.—The capability of the He-beam scattering as a method to study directly the migration of low-coverage adsorbates on a single-crystal surfaces is demonstrated. The method is based on the unique feature of the He scattering to distinguish between molecules adsorbed on defect-free areas and at defect sites. The very large scattering cross section of adsorbed CO for He beams makes it possible to measure the CO migration at very low coverages and also to study the island formation. The activation energy for CO migration on the Pt(111) surface is 7 kcal/mole. There is no CO island formation on a defect-free Pt(111) surface at low CO coverage (~1.5%) between 120 and 400 K.

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

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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 $|V_{zz}(\text{surface})| = 5.6(6)\times10^{17}$ V/cm^2 with an orientation perpendicular to the surface. This is a drastic enhancement of the field gradient compared with bulk by a factor $|V_{zz}(\text{surface})/V_{zz}(\text{bulk})| \approx 4$. The result is discussed in a simple one-Wigner-Seitz-cell model.

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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 quasi-two-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 ^{57}Fe, 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 silver[6] substrates have been noticed in ^{57}Fe 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 ^{111}In 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 ^{111}In (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 transfered 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