

## Off-Specular Coherent and Incoherent Elastic Scattering from Cu(001) and Adsorbed Layers of CO and Xe

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Coherent and incoherent elastic scattering of He was observed from Cu(001) and adsorbed layers of CO and Xe. It is shown that specular and off-specular elastic scattering can yield insight into adsorption mechanisms at low coverages. The variation of incoherent elastic scattering with coverage shows different behavior for CO (random) and Xe (island) adsorption. A maximum appears in the incoherent elastic for CO as predicted theoretically for site adsorption.

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The recent development of energy analyzers for low-energy beams of light atoms has shown how information on surface modes of vibration can be extracted by measuring the one-phonon inelastic component.<sup>1,2</sup> Surface modes of vibration have been measured for both ionic crystals and a metal (Cu). In addition, localized surface modes have been detected for adsorbed layers of Xe<sup>3</sup> and Kr.<sup>4</sup> In addition to the inelastic component, an off-specular elastic component was always detected in He scattering from Cu(001) as well as Ag(001)<sup>5</sup> which in the case of Cu comprised a reasonable fraction of the scattered intensity.<sup>6</sup> This elastic incoherent component was thought to result from features such as random surface steps in the same manner that Henzler's<sup>7</sup> calculations yielded broadening of low-energy electron-diffraction (LEED) spots depending on surface step intensity. The off-specular elastic peak still persisted during progressive adsorption of gases on Cu(001), (e.g., CO, Xe, Kr, and CH<sub>4</sub>) as the main specular peak fell in intensity. Further, this elastic incoherent peak varied in intensity depending upon different adsorbed gases and therefore upon the mechanism for the gas adsorption. For site adsorption, Levi, Spadacini, and Tommei<sup>8</sup> predicted a maximum as a function of coverage. We demonstrate that energy analysis yields information on modes of vibration but in addition an important feature in the study of adsorption models can be the incoherent elastic component. The gases chosen to show differences in the mechanism of adsorption on Cu were CO and Xe, the former showing irreversible strong adsorption while Xe could be desorbed, consequently indicating a more mobile adsorbed state. Both CO (Ref. 9) and Xe (Ref. 10) have been studied widely in the adsorbed state on Cu(001) by LEED, surface potential, and isotherms, and CO by electron-energy-loss spectroscopy (EELS).<sup>11</sup> The present work also shows

inelastic features of adsorbed CO not resolved by EELS. The experimental arrangement was similar to that described previously<sup>12</sup> and the temperature of the Cu (16 K) and the energy of the He beam (22.6 meV) similar to that described recently.<sup>6</sup>

Figure 1 (lower curve) shows typical results obtained by scanning<sup>12</sup> the analyzer diffraction peak for a fixed angular position of the clean Cu sample. The analyzer direction was fixed at 130° to the incident beam, i.e.,  $\varphi_0 + \varphi_s = 50^\circ$ , where  $\varphi_0$

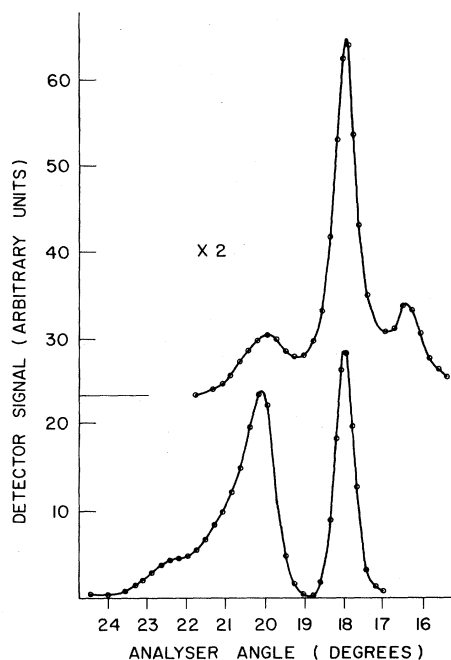


FIG. 1. Scans obtained by rotating the analyzer for fixed positions of the Cu. The lower curve shows an inelastic band on the left-hand side and an off-specular elastic peak for clean Cu;  $\varphi_0 = 33^\circ$ . The top curve shows a similar scan for CO adsorbed on the Cu surface. The elastic peak was still in evidence. Energy loss and gain peaks of 3.5 meV appear;  $\varphi_0 = 33.1^\circ$ .

and  $\varphi_s$  are the glancing angles of incidence and scattering, respectively. The paths between the analyzer and sample, and the analyzer and detector, respectively, include an angle of  $100.5^\circ$ . The peak on the left of Fig. 1 (lower curve) is the band of energy-loss events resulting from one-phonon inelastic processes.<sup>6</sup> Energy-loss events were only observed in the subspecular region and have been described elsewhere.<sup>2</sup> The peak on the right of the scan was the off-specular elastic peak ( $\varphi_0 = 33^\circ$ ) always obtained with Cu. This elastic peak was not confined to the subspecular region but covered a wide angular range and as such represented a sizable fraction of the total flux [the peak was approximately  $5 \times 10^{-4}$  of the (00) peak]. The origin of this peak was probably an incoherent elastic component generated by defects such as monatomic steps on the surface. Surface steps on metals are a common feature (both regular and irregular, especially on using ion-bombardment techniques) as has been pointed out by Henzler<sup>7</sup> who performed calculations to show the broadening of LEED patterns resulting from various step orientations and percentages of step-edge atoms. A similar elastic component was observed for Ag(001) (prepared in a similar way) in our previous energy-analysis system.<sup>5</sup> Toennies *et al.*,<sup>2</sup> in the case of LiF, found little evidence for an off-specular elastic peak except in the region of the crystal edge where it was postulated that steps were the cause of this component. The upper curve of Fig. 1 shows that the elastic component persisted even with a monolayer of CO on the surface. Figure 2 shows the variation of the elastic (00) peak (closed circles) as the Cu was progressively covered with CO. On a semilog scale, the peak fell linearly almost up to a coverage ( $\theta$ ) of 0.3 (estimated from the CO exposure and unity sticking) which is the region of the minimum of the curve. For higher exposure, the (00) peak increased by a factor of 2. Further, the (00) peak increased spontaneously for a number of minutes at each point (after the CO beam was switched off) indicating that some slow reorganization was occurring, perhaps due to dipole-dipole repulsion between adjacent sites. During CO adsorption, a broad diffraction peak developed from a diffuse sloping background. The peak started to appear at  $\theta = 0.4$  and reached an intensity of  $10^{-11}$  unit (on Fig. 2) along with decreasing halfwidth ( $1.5^\circ$ ) at  $\theta \approx 0.8$ . The sticking coefficient during adsorption was found by Tracy<sup>9</sup> to be unity who also found that at 77 K,  $9 \times 10^{14}$  molecules could be accommodated. As the ad-

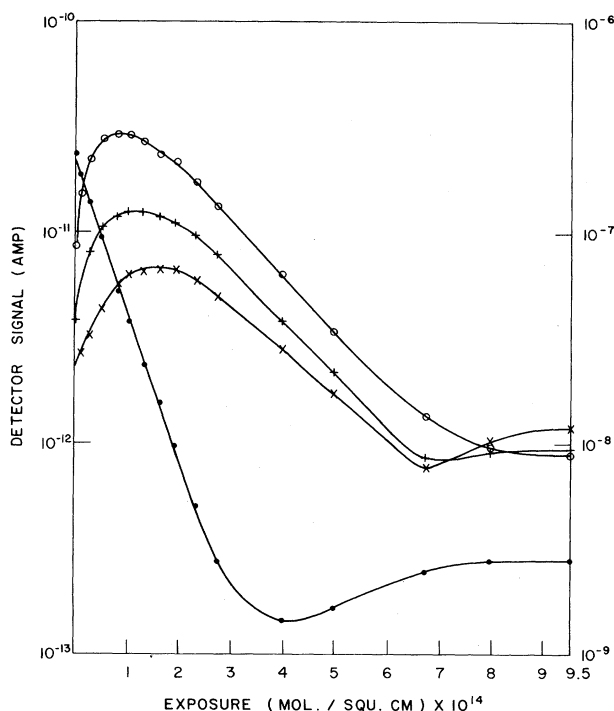


FIG. 2. Variation of the (00) peak height (closed circles) as a function of the number of CO molecules striking the crystal (ordinate on right). In the region  $\theta = 0.5 - 1$ , the beam increased with time after the CO beam was stopped indicating a reordering. The three other curves show the variation of the off-specular elastic peak as a function of the exposure to CO molecules for positions  $7.6^\circ$ ,  $12.9^\circ$ , and  $16.1^\circ$  from the (00) peak (top to bottom).  $\theta = 1$  for  $9 \times 10^{14}$  mol/cm<sup>2</sup>.

sorption was irreversible on heating, it would appear that the process followed a site adsorption mechanism where the CO did not migrate from the point of condensation on the surface, except perhaps for  $\theta > 0.5$  where repulsion overcomes the site-to-site energy barrier. For such a site model, Levi, Spadacini, and Tommei<sup>8</sup> have predicted the presence of an elastic incoherent component which should cover a wide angular range and be centered at the (00) peak. The variation of such an off-specular elastic component during adsorption is shown in the three other curves of Fig. 2. It is clear that at angles of  $7.6^\circ$ ,  $12.9^\circ$ , and  $16.1^\circ$  (top to bottom) from the (00) peak, this elastic component increased (from the value for the clean Cu) by a factor of 3, showed a maximum, and then fell to a minimum value in the region of monolayer completion. The maxima appear at values of  $\theta$  in the region  $0.1 - 0.15$  depending upon the angle from the (00).

The maxima tended to higher values of coverage as the glancing angle of incidence increased. Levi predicted a maximum at  $\theta = 0.5$ , the difference perhaps being due to the shadowing effect—see below.

Figure 3 shows the results for a similar experiment for Xe. The curve (closed circles) shows the variation of the (00) peak on progressive adsorption and was quite different in shape. The initial slope was a factor of 4.3 smaller. At about  $\theta = 0.6$ , the rate of fall increased dramatically before leveling near  $\theta \sim 1$  ( $\theta = 1$  at  $5.7 \times 10^{14}/\text{cm}^2$ ).<sup>13</sup> A diffraction peak developed on adsorption which was larger and always narrower ( $0.5^\circ$ ) than for CO. It increased from  $1 \times 10^{-11}$  to  $3 \times 10^{-11}$  unit for the range  $\theta = 0.1 \rightarrow 1$ . The sticking coefficient of Xe is high at higher temperatures,<sup>13</sup> e.g., 0.9 at 77 K, and in this instance the (00) peak fell to its lowest level for a coverage near a monolayer. It seems therefore that the differences in the

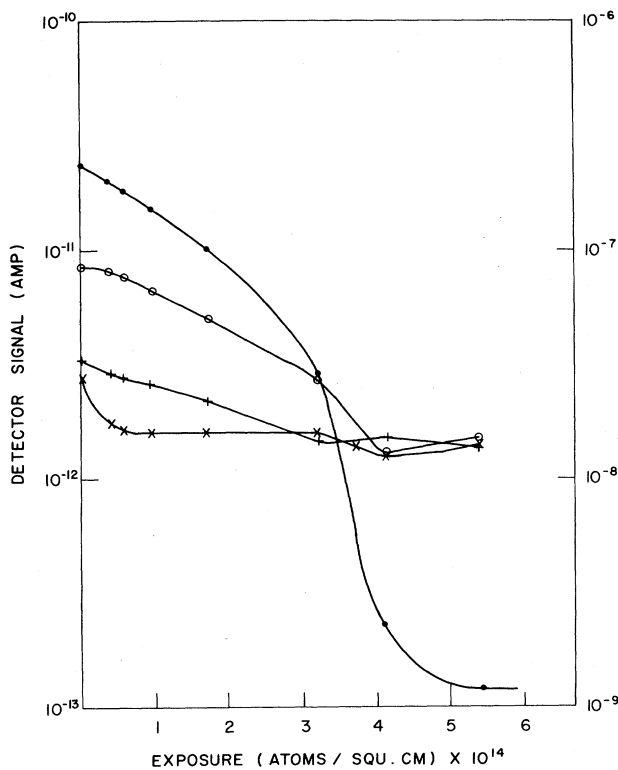


FIG. 3. Similar to Fig. 2, for the Xe atoms. The (00) peak's (closed circles) initial slope was about a factor of 4 smaller but the slope changed rapidly for higher coverages. The sticking coefficient was assumed to be unity and the monolayer coverage was  $5.7 \times 10^{14}$  a/cm<sup>2</sup> (Ref. 13). The other three curves show the variation of the off-specular peak with coverage for the same positions as in Fig. 2.

shapes of the curves yield information on the mechanism of adsorption. To indicate further differences, the other three curves of Fig. 3 show the off-specular peak for the same positions as the CO results. No increase occurred in this case and at all points the elastic component fell to a minimum value (from that for the clean Cu) for larger  $\theta$ . Small differences in the values of elastic peaks for large  $\theta$  in the case of CO and Xe are probably due to diffraction effects from the monolayer.

From the initial slope versus coverage for CO, it was found that for 1% coverage, the (00) peak fell by 20% indicating that the effective scattering cross section at the surface was high. This high value arose from the projected area of isolated CO on the surface which produced a large scattering site for the incident waves. Therefore, for random site adsorption, a large part of the Cu surface was removed, hence the steep slope for CO adsorption. Further, the number of random sites was high to yield the increase in the incoherent scattering.

In the case of Xe, where a sharper diffraction peak appeared at much lower  $\theta$ , and where the atoms were more mobile<sup>13</sup> (adsorption reversible), clusters of Xe atoms arose on the surface. The effective area of the surface covered was therefore smaller, so that the initial slope of the (00) curve was not as large as in CO, and became steeper only when islands of nuclei began to coalesce or a phase transition occurred. The islands would, in this case, yield more coherent scattering (hence diffraction) and less incoherent (off-specular) scattering on adsorption. No increase in the off-specular peak was found even for small exposure which might be expected for Xe adsorption on active sites and steps.<sup>14</sup>

We therefore show that the incoherent and elastic scattering can yield important information on adsorption mechanisms at low coverages especially if placed on a quantitative basis. Order-disorder transitions could well be detectable with use of this technique.

The upper curve of Fig. 1 shows an analyzer scan of CO on Cu. Energy-gain and -loss events appeared similar to a film of Xe.<sup>6</sup> The peaks show an energy change of 3.5 meV which is much smaller than found in EELS studies, e.g., 43 meV for Cu-CO bond and other modes (14.5 meV) thought to be associated with zone-boundary surface modes. This energy (3.5 meV) was also much smaller than estimated bending modes for CO on Ni.<sup>15</sup> It is therefore probable that the peaks

are due to coupling between the CO and lattice modes in the Cu to yield a resonant mode.<sup>16</sup> The inelastic scattering from CO was independent of incident conditions similar to Xe (Ref. 6) and Kr.<sup>4</sup>

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## Model for the Equation of State of Condensed Matter in the "Intermediate" Pressure (about 0.5–10 TPa) Region

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A model for the equation of state of condensed matter in the "intermediate" pressure region (0.5–10 TPa) is proposed. The dominant pressure and thermal ionization effects are simulated through a modification of Saha's ionization theory. The pseudopotential method which includes core ionization effects is used to obtain the cold and lattice thermal contributions. The model is applied to Al and Mo.

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Most  $P$ - $V$  data from shock compression experiments are limited to pressures below about 0.5 TPa.<sup>1,2</sup> The various theoretical equation-of-state models are also adequate either for this "experimental" region<sup>3,4</sup> or for the high-density "Thomas-Fermi-Dirac" (TFD) region<sup>5</sup> involving pressures and temperatures greater than 10 TPa and 100 eV, respectively.

Recently, some experimental data have been generated in the "intermediate" region (about 0.5–10 TPa). Trainor *et al.*<sup>6</sup> have used laser energy deposition to achieve shock velocities corresponding to pressures up to 1.8 TPa in aluminum. By means of shocks produced by underground nuclear

explosions, Hugoniot equation-of-state points have been measured by Ragan and co-workers<sup>7,8</sup> for molybdenum at 2.0 and 4.9 TPa and for uranium at 6.7 TPa and by Al'tshuler *et al.*<sup>9</sup> and Podurets *et al.*<sup>10</sup> for a number of materials in the range 1–5 TPa.

Some theoretical attempts have also been made recently to develop an equation-of-state model in the intermediate region by incorporating shell structure effects in TFD theory.<sup>11,12</sup> Liberman<sup>13</sup> has proposed a self-consistent spherical TFD model in which the potential is in the muffin-tin form. Ross<sup>14</sup> has extended Ashcroft's liquid perturbation theory<sup>15</sup> to dense, partially ionized