

(Van Nostrand, Princeton, New Jersey, 1945)]. The corresponding *lattice* modes for H occupying a C_{2v} point-group bridge site on W(100) are equivalent to a motion of the H atom *perpendicular* to the surface (A_1 symmetric stretch) and two *lateral* displacement modes (B_2 asymmetric stretch and a second A_1 out-of-plane "bending" mode). The latter two lateral modes are only resolved for off-specular scattering (see text).

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Random Occupation of Adsorption Sites in the $c(2 \times 2)$ Structure of CO on Fe{001}

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A low-energy electron-diffraction intensity analysis of the Fe{001} $c(2 \times 2)$ -CO structure confirms the results of photoemission studies by other workers suggesting dissociation of the CO molecule. The data are fitted well by a model with random occupation of four-fold symmetrical sites by carbon and oxygen atoms in a $c(2 \times 2)$ configuration, similar to that proposed earlier by Felter and Estrup and by Riwan, Guillot, and Paigne for Mo{001} $c(2 \times 2)$ -CO.

The adsorption of carbon monoxide on iron has been recently studied by photoemission with both polycrystalline^{1,2} and single-crystalline³ substrates. In both cases, the experimental results have indicated that the CO molecule dissociates upon adsorption. In addition, the work of Rhodin and Brucker³ has shown that on Fe{001} the adsorbed layer is ordered and forms a $c(2 \times 2)$ structure. We have also observed such a superstructure in our own adsorption experiments of CO on Fe{001}. We wish to report here the results of a LEED (low-energy electron-diffraction) intensity analysis of this structure, which reveals an atomic arrangement not heretofore confirmed on any other surface.

The experimental and theoretical details will be reported elsewhere. Here we will mention only that we have collected, for the purposes of structure analysis, a total of 23 LEED spectra: five at normal incidence, ten at polar angle $\theta = 10^\circ$, and eight at $\theta = 20^\circ$, all for an azimuth angle $\varphi = 0^\circ$. The intensity calculations were done with a computer program that includes in a single surface layer the three subplanes of carbon, oxygen,

and uppermost iron atoms, and calculates all multiple scatterings within this composite layer in the angular-momentum representation. The multiple scattering between this composite layer and the bulk layers is then computed in the plane-wave representation. Exploratory calculations were made with five phase shifts and 58 beams, while the final calculations for the best model were made with eight phase shifts and 58 beams for energies up to about 100 eV, 74 beams up to 150 eV, and 90 beams up to 200 eV.

Following the photoemission results, only structural models involving dissociated CO were tested. However, it was confirmed in the initial stages of the analyses that the model of CO molecules perpendicular to the surface with the C end does *not* produce agreement with experiment. Since a recent LEED analysis has established that oxygen chemisorbed on Fe{001} in a 1×1 structure resides in the fourfold symmetrical hollows,⁴ it was assumed that the latter would also be the adsorption sites for O in the Fe{001} $c(2 \times 2)$ -CO structure. Thus, the models to be tested involved 0.5 monolayer of O always in the four-

fold symmetrical sites in a $c(2 \times 2)$ configuration, while C was assumed to lie, also in a $c(2 \times 2)$ configuration, in one of five possible sites: (a) in the remaining fourfold symmetrical sites left vacant by the oxygen adatoms (either coplanar or not coplanar with the latter; see Fig. 1), (b) in the twofold symmetrical bridge sites across two adjacent substrate atoms, (c) atop substrate atoms, (d) in the tetrahedral interstitial sites, and (e) in either of the octahedral interstitial sites between the first and the second iron layers. None of these models produced acceptable agreement with the experimental spectra.

It was discovered, however, that satisfactory

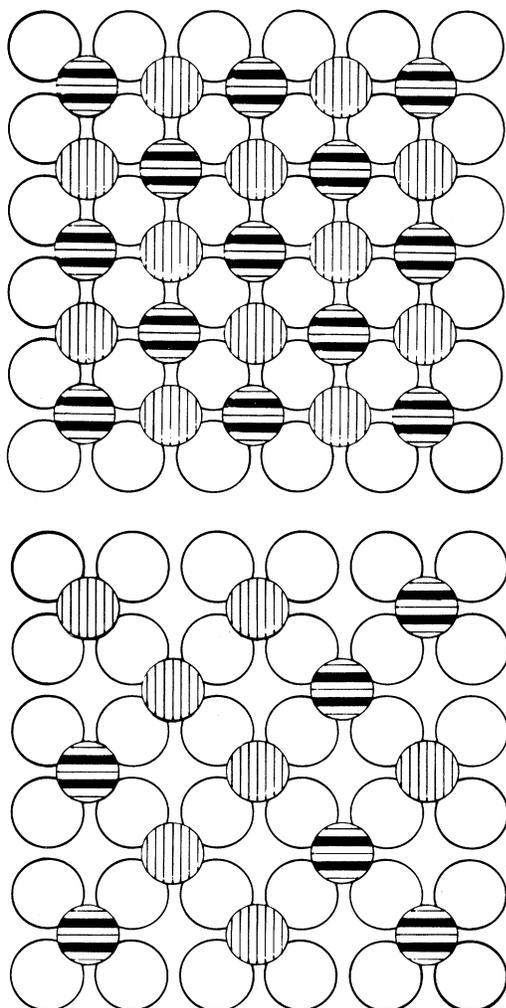


FIG. 1. Top, C atoms (vertically shaded circles) and O atoms (horizontally shaded circles) are both located in the fourfold sites. Other models tested involve C atoms in the bridge sites or on top of the substrate atoms (open circles). Bottom, random-occupation model.

agreement can be achieved with models involving either oxygen *only* or carbon *only*, arranged in a $c(2 \times 2)$ net on fourfold symmetrical sites. The differences between the spectra calculated either way are only minor. This observation can be interpreted in two ways. The first (and less probable) is that, upon adsorption and dissociation of CO, the O atoms conglomerate into regions, or islands, in which they form an $\text{Fe}\{001\}c(2 \times 2)\text{-O}$ structure, while the C atoms coagulate in separate islands in which they form an $\text{Fe}\{001\}c(2 \times 2)\text{-C}$ structure. If the surface were half covered by one type and half by the other type of island, for example, and the islands were at least as large as the electrons' coherence length, in linear dimensions, then the observed LEED spectra would result from the average of the corresponding LEED spectra of the two coexisting structures. Figure 2 shows, for three spectra at normal incidence, that such an average differs very little from either component (top three curves in each panel), and is therefore in satisfactory agreement with experiment. That LEED spectra obtained from chemisorbed oxygen or/and carbon (or/and nitrogen) are very similar to one another has been observed before.⁵ It is interesting to note, incidentally, that the LEED spectra calculated for a hypothetical $\text{Fe}\{001\}c(2 \times 2)\text{-N}$ structure (fourth curve from the top in each panel of Fig. 2) are practically indistinguishable from those obtained by the average of the O and C structures or for either one of these structures separately.

The second (and more probable) interpretation of the results is that carbon and oxygen atoms occupy randomly fourfold symmetrical sites in a $c(2 \times 2)$ configuration (see Fig. 1). Note that in this model (which we may call, for brevity, the random-occupation or RO model), just as in the preceding island model, the *total* surface coverage is $\frac{1}{2}$ monolayer, e.g., $\frac{1}{4}$ from C and $\frac{1}{4}$ from O, whereas in all other models listed above the total coverage is 1 monolayer, $\frac{1}{2}$ from C, $\frac{1}{2}$ from O.

Some evidence supporting models with the smaller coverage is provided by Auger-electron spectroscopy (AES). If we compare the ratio $\text{O}_{515}/\text{Fe}_{650}$ between the intensities of doubly differentiated AES lines of oxygen at 515 eV and of Fe at 650 eV, as observed on the $\text{Fe}\{001\}1 \times 1\text{-O}$ structure,³ with the corresponding ratio observed presently on the $\text{Fe}\{001\}c(2 \times 2)\text{-CO}$ structure, we find that in the latter the oxygen concentration is only about $\frac{1}{3}$ of the former, or about 0.3 monolayer. Using this information, together with the observed

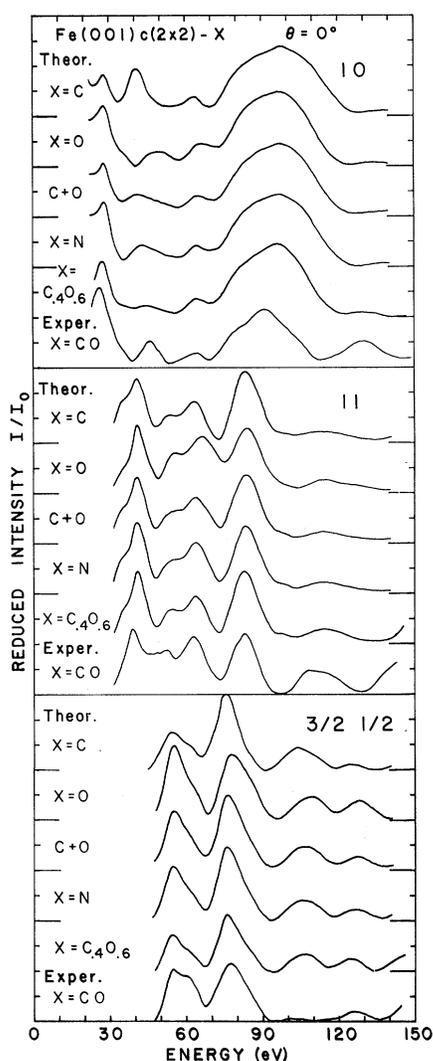


FIG. 2. Calculated and observed 10, 11, and $\frac{3}{2} \frac{1}{2}$ LEED spectra at normal incidence. In each panel, starting from the top, the curves are as follows: calculated for $\text{Fe}\{001\}c(2 \times 2)\text{-C}$; calculated for $\text{Fe}\{001\}c(2 \times 2)\text{-O}$; 50-50 average of the latter two; calculated for $\text{Fe}\{001\}c(2 \times 2)\text{-N}$; calculated for an "averaged" atom ($\text{C}_{0.4}\text{O}_{0.6}$); experimental for $\text{Fe}\{001\}c(2 \times 2)\text{-CO}$.

ratio of C and O AES lines and with the measured values of the ionization cross sections⁶ of C and O, we calculate a carbon concentration of about 0.2 monolayer. These results are probably not reliable enough to distinguish with certainty between a 60-40 ratio and a 50-50 ratio of O to C, but they ought to be reliable enough to suggest that the *total* surface coverage is much closer to $\frac{1}{2}$ than to 1 monolayer.

Further support for the plausibility of the RO

model comes from the studies of the $\text{Mo}\{001\}c(2 \times 2)\text{-CO}$ structure that were done independently by Felter and Estrup⁷ and by Riwan, Guillot, and Paigne.⁸ In this case, LEED and AES observations indicated that the oxygen and carbon concentrations were one half of those found in the $\text{Mo}\{001\}c(2 \times 2)\text{-O}$ and the $\text{Mo}\{001\}c(2 \times 2)\text{-C}$ structures, respectively. Felter and Estrup specifically suggested the RO model for the CO structure.⁷ Unfortunately, a structure analysis of the latter was never carried out.

Our theoretical treatment of the RO model is the following. We assume that carbon and oxygen are coplanar, i.e., that they are located at the same distance, in the fourfold symmetrical sites, from the substrate atoms—an assumption that is based upon the fact that calculations for either the carbon or the oxygen structure alone indeed agree best with experiment for the same value of the adsorbate-substrate distance. We then replace both atoms with an "averaged" atom whose scattering amplitude is obtained from an average of the scattering amplitudes of the two in a way similar to that in which the atomic vibrations are usually handled.⁹ This "averaged" atom, which we may call (C_xO_{1-x}), occupies the fourfold symmetrical sites in the $c(2 \times 2)$ configuration, and the LEED spectra are then calculated for this average atom in the usual way (see above). Figure 2 depicts the spectra pertaining to a ($\text{C}_{0.4}\text{O}_{0.6}$) atom—those produced by a ($\text{C}_{0.5}\text{O}_{0.5}$) atom are practically identical. The adsorbate-substrate interlayer spacing was taken to be 0.48 Å, corresponding to an effective radius of 0.67 Å for the "averaged" atom. This value lies below the ranges 0.71–0.78 Å and 0.70–0.88 Å found for O and C, respectively, on other surfaces,¹⁰ but is larger than the effective radius 0.48 Å recently determined for both O and C in the $\text{Ti}\{0001\}p(2 \times 2)\text{-CO}$ structure.¹¹ The agreement between calculated and observed LEED spectra is satisfactory not only for the three normal-incidence beams shown in Fig. 2 but for all the remaining twenty beams available. However, the possibility of a slight expansion of the first substrate interlayer spacing is not ruled out. A refinement of this structure, involving *r*-factor analysis, will be published elsewhere.

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Absence of Anomalous Kapitza Conductance on Freshly Cleaved Surfaces

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The reflection coefficient of 290-GHz phonon pulses between LiF or NaF and liquid helium was measured with surfaces prepared *in situ* by cleaving at 1 K. Nearly 100% reflection was found, thus demonstrating the absence of the anomalous Kapitza conductance in contrast to all previous experiments.

The process of heat transfer between solids and liquid helium has received great interest in recent years.¹ The Khalatnikov model² of phonon transmission under strong acoustic mismatch can explain the results of both thermal conductivity experiments below 0.1 K on vacuum-annealed surfaces³ and the high reflection coefficient observed in phonon experiments below 20 GHz.⁴ At higher temperatures or higher phonon frequencies, however, the energy transfer was too large by about two orders of magnitude in all experiments so far. This phenomenon is commonly referred to as the anomalous Kapitza conductance. Its origin is still unknown, although several theoretical models have been suggested.^{4,5}

Before proposing specific models, it is important to know whether the effect is intrinsic to an ideal solid surface or it is caused by irregularities. This question has not been answered yet. Although in some experiments cleaved surfaces were used, all of these had been exposed to air. In one attempt to use ultrahigh-vacuum (UHV) conditions with ion-bombarded surfaces, only 10^{-8} Torr was maintained for several hours before the measurement.⁶ Nevertheless, the Kapitza conductance appeared to be reduced. We wish to report here on the first experiments on surfaces prepared by cleaving at 1 K *in situ*. Surprisingly, the anomalous Kapitza conductance is almost absent on these nearly ideal surfaces.

The experimental setup was similar to that used in our previous work,⁷ except for the crystal holder shown in the inset to Fig. 1. A crystal of LiF or NaF was sealed into a vacuum chamber so as to form a window. Onto the outside surface of the crystal, superconducting tunneling junctions were evaporated as generator (Sn) and detector (Al) of monochromatic phonon pulses of 290 GHz.⁸ The chamber was immersed in the helium bath. By this geometry, stable conditions were maintained for the junctions.

Inside the chamber, a razor blade had been carefully adjusted to a (100) cleavage plane of the crystal far from the junctions. The blade could be actuated by a screw which also served as a baffle to the filling line on top of the chamber. In a typical run, the chamber was pumped at room temperature for 1 h with the screw out of position, and then cooled down with the screw in position. At 1 K, the seal was tested by a helium-leak detector. In the absence of a helium leak, an excellent vacuum (better than 10^{-12} Torr) is expected.

Figure 1 shows the results of an experiment with LiF. The dash-dotted trace is the detected phonon signal versus time before cleaving. Two reflected pulses are seen on top of a background due to bulk scattering in LiF. The direction of the group velocity as determined by the junction geometry was about 3° away from the [100] axis.