

Determination of Atomic Positions in the $C(2 \times 2)$ Oxygen Structure on a Nickel (100) Surface by a Dynamical Low-Energy Electron-Diffraction Method

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The dynamical method of low-energy electron-diffraction intensity analysis has been applied to the system of $C(2 \times 2)$ oxygen on nickel(100). This system differs considerably both geometrically and chemically from the sodium-on-nickel system previously reported. The diffraction data are consistent with a model where oxygen sits in a layer displaced normal to the surface by $d = 1.5 \pm 0.1$ Å from the center of the top layer of nickel atoms. Oxygen atoms sit above pyramidal hollows in the nickel layer below.

In two previous papers^{1,2} a determination of atomic positions in the $C(2 \times 2)$ sodium structure on a nickel (100) surface was made by comparing theoretical and experimental low-energy electron-diffraction (LEED) intensities, establishing the practicability of the technique to an accuracy of ± 0.1 Å. In this Letter we report on atomic positions in a very different system: the $C(2 \times 2)$ oxygen structure on a nickel (100) surface. Elementary geometric considerations differentiate strongly between sodium and oxygen. From lattice constants of bulk nickel, sodium, and nickel oxide we deduce atomic radii of 1.25, 1.86, and 0.84 Å for nickel, sodium, and oxygen, respectively. The much smaller oxygen atom suffers less geometric restriction on the nickel (100) surface than does sodium. Also, chemically the oxygen and sodium cases are different. Nickel and oxygen are known to form a high-melting-point, partly covalent compound, and the larger bonding energy involved raises a larger number of possibilities for the $C(2 \times 2)$ structure.

The small radius of oxygen, plus the strong character of nickel-oxygen bonds, means that even if it is known what general configuration the atoms take, distances are not fixed accurately. For example, taking the radii above and sitting oxygen in the pyramidal configuration above hollows in the nickel layer leads to a value for the vertical spacing between planes of oxygen and nickel atoms of $d = 1.13$ Å. Substituting the oxygen radius found in O_2 (0.60 Å) gives $d = 0.57$ Å,

a difference of 0.56 Å.

The system is a technically interesting one as a prototype of oxidation initiation studies in general, and has been much investigated already by Farnsworth and Madden,³ Park and Farnsworth,⁴ MacRae,⁵ and May and Germer⁶ using LEED techniques, and by Hagstrum and Becker⁷ using ion-neutralization spectroscopy. None of this work has given a determination of the geometry of the system, though Hagstrum and Becker believed that oxygen must be reasonably well buried in the nickel surface, either by replacing atoms in the top nickel layer, or by sitting deep in the hollows in the nickel layer.

Differences between LEED experiments on the two systems are less striking than geometry and chemistry might imply, but there are important differences. In many respects oxygen structures are easier to work with. The stronger bonds make for smaller thermal vibrations, and it is a decided advantage not to have large thermal corrections to make in systems where there are virtually no theoretical calculations for vibrational amplitudes. Also, oxygen being smaller than sodium and less deformable, the associated ion-core scattering is available with greater accuracy for oxygen atoms at surfaces. Another source of error that is reduced is in the correlation potential acting between ion cores. In the case of sodium on nickel we assumed that it took a constant value through the sodium layer and estimated that errors of around 0.1 Å were thereby intro-

duced. For oxygen on nickel, the oxygen layer is almost certainly much closer to the nickel layer, and the correlation potential will not have varied by so much over the much shorter distance.

On the other hand, greater variety of feasible structures for oxygen on nickel may complicate structural determination. Structures cannot be found by direct inversion of LEED data; trial structures must be postulated and their spectra compared with experiment. In principle the method is always open to the criticism that even though a structure gives agreement with experiment, another might give equally good agreement. There is no uniqueness theorem. In practice it is highly improbable that two structures would give the same spectra for all diffracted beams.

Our method of calculation has been described in other papers,^{2,8} and we shall not repeat it here except to say that ion-core scattering is determined from first principles and the constant potential between ion cores is determined in its real part from work-function measurements and band-structure calculations, and in its imaginary part from peak widths in the clean nickel spectrum. In this work we fitted peak-width data for clean nickel with an analytic function of energy (given in Hartrees),

$$V_{oi} = -0.04 - \frac{0.107}{1 + \exp[-5(E - 1.3)]},$$

rather than the step function used in earlier papers. Both treatments are consistent within the accuracy of the data, but a continuous function has calculational advantages. *Thus no parameters other than the geometry we wish to find are available to us in the overlayer problem.* We neglect temperature effects and stay at low energies to avoid their more serious consequences.

Adsorption of oxygen on nickel has been the subject of a number of investigations as mentioned above. The adsorption kinetics, i.e., the dependence on oxygen pressure and substrate temperature for the formation of the ordered oxygen surface structures, has been carefully studied by LEED. Our purpose was to obtain useful experimental diffraction intensities from the nickel-oxygen system, and it was of interest to know if conditions of formation would influence the intensity data. Preparation of the clean well-ordered nickel surface and our methods to determine absolute diffraction intensities and work function changes have been described previously.² The ambient pressure in the diffraction chamber was below 10^{-11} Torr, and the purity of the oxygen

gas was better than 1:1000, the main contaminant being carbon monoxide. We found that oxygen exposures in the range 2.10^{-5} – 8.10^{-5} Torr sec at 200°C and 1.10^{-8} – 1.10^{-7} Torr oxygen pressure produced a $C(2\times 2)$ structure that yielded essentially identical intensity data. Annealing at 300°C improved the contrast and the absolute beam intensity somewhat, but peak positions were not influenced. This was also the observation after formation at different substrate temperatures in the range 25 – 225°C . Thus we feel confident that the conditions of formation of the $C(2\times 2)$ oxygen structure do not influence peak positions in the intensity data by just absolute intensities, and contrast to a smaller extent. We found in the energy range explored that peak positions were reproducible to better than 0.5 eV and peak intensities to about 25%. For the well-annealed $C(2\times 2)$ structure the work function was increased by 0.3 eV.

As a final check our experimental curves have been compared with those measured by Demuth and Rhodin.⁹ The two sets of data are essentially identical.

We have made calculations with oxygen atoms on several different sites, each consistent with the $C(2\times 2)$ LEED pattern: for oxygen atoms directly above nickel atoms in the layer below, in bridge sites between nickel atoms (and equal numbers of domains with bridge sites at right angles to each other), for sites above hollows in the layer of nickel atoms, and for a reconstructed configuration in which every other nickel atom in the top layer is replaced with an oxygen atom.

We observed in the sodium overlayer work that the 00 beam was insensitive to lateral displacements of the overlayer, a conclusion also valid for the iodine on silver(111) structure.¹⁰ A similar, though less marked insensitivity was seen in the present system. Thus the vertical spacing of the overlayer is to be had from the 00 beam, independently of whether the correct lateral assignment has been made. Lateral displacements and additional checks on the vertical displacements are to be deduced from nonspecular beams.

We find that the experimental data are best fitted by a vertical separation between the center of the last nickel layer and the oxygen layer of $d = 1.5 \pm 0.1$ Å. Best agreement in the nonspecular beams was found for oxygen atoms situated above the hollows. Figure 1 shows comparison of the best theoretical curves with experiment.

A point that we stress is that a general feature of comparisons between experiment and theory

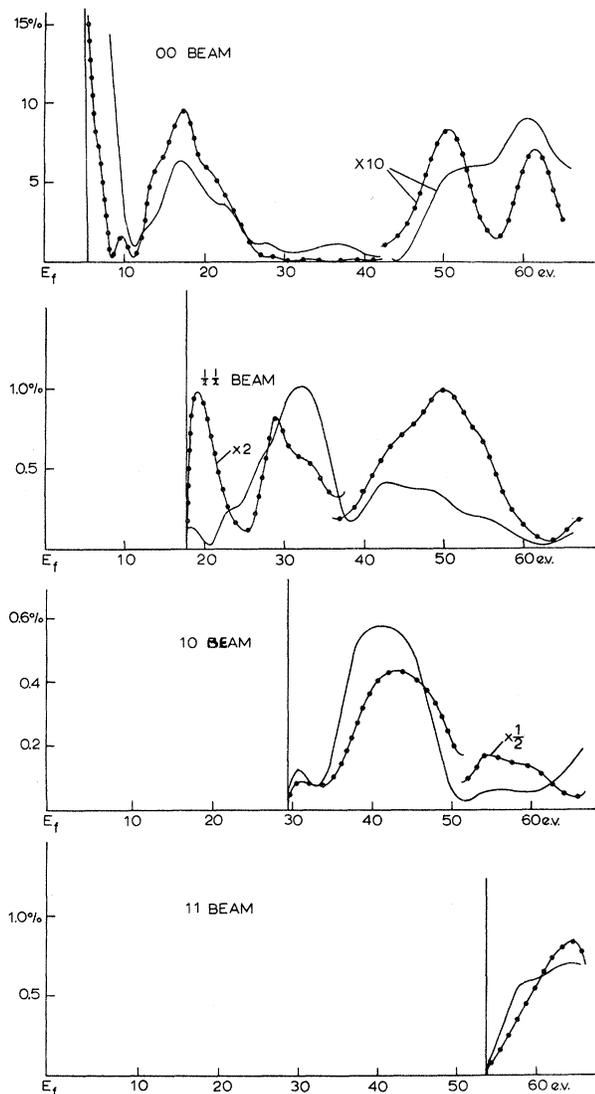


FIG. 1. LEED spectra taken at normal incidence from a $C(2 \times 2)$ oxygen structure on a nickel (100) surface. Solid line, experiment; solid line with dots, theory for oxygen atoms placed over hollows in the top nickel layer, $d = 1.5 \text{ \AA}$.

is the good agreement of peak positions (to within 1 or 2 eV) and the relatively poor agreement of intensities (to within 50% for a clean nickel surface in the energy range we use). This is because the less well-known parameters, such as thermal vibrations, affect intensities much more strongly than peak positions. Consequently, much greater weight must be given in structural determinations to agreement of energies at which structure occurs than to intensities, which we require to agree only in a qualitative sense.

Carrying this philosophy to its extreme conclu-

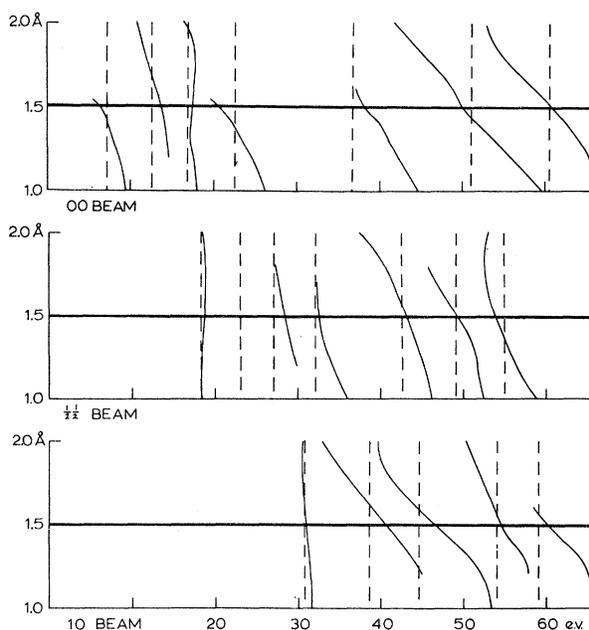


FIG. 2. Solid line, energies at which peaks in theoretical spectra occur (coordinate) as functions of d (ordinate). Oxygen atoms are placed over hollows in the top nickel layer. Dashed line, experimental energies of peaks.

sion we have made a decomposition of experimental and theoretical curves into Lorentzian peaks,

$$I(E) = \sum_j \frac{|A_j|^2}{(E - E_j)^2 + V_{0i}^2},$$

recognizing that structure has an intrinsic width of $2V_{0i}$. Figure 2 shows peak energies E_j plotted against vertical displacement of the oxygen layer above the pyramidal hollows. Experimental peak positions are shown by vertical bars. Note that every experimental peak can be associated with a theoretical one except for the small peak at 22.5 eV in the $\frac{1}{2} \frac{1}{2}$ beam. Further, at the assigned spacing of 1.5 \AA all eighteen theoretical positions agree with experimental ones within $\pm 2 \text{ eV}$. It will be seen from Fig. 2 that no other spacing gives comparable agreement, and this was also the case for other lateral positionings.

Our conclusion that the oxygen sits above pyramidal hollows in the top nickel layer, with a vertical displacement of $1.5 \pm 0.1 \text{ \AA}$ implies a nickel-oxygen bond length of $2.3 \pm 0.1 \text{ \AA}$ in nickel oxide. Thus, as with the sodium on nickel structure, the concept of atomic radius holds to within a few tenths of an angstrom. No obvious interpretation of the structure in terms of covalent bonds is possible, oxygen having four nickel nearest neigh-

bors. Similarly, considerations of electronegativity differences, which would imply that oxygen be negatively charged, seem not to be relevant: For our configuration even a small charge on the oxygen would be inconsistent with the observed work-function change of 0.3 eV. It was this fact that led Hagstrum and Becker⁷ to postulate a structure in which nickel is coplanar with oxygen, allowing charge transfer without a dipole moment. However, such a model was found incompatible with the LEED data. It would seem that for an understanding of surface chemistry some modification of traditional chemical concepts will be required.

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Specific-Heat Anomalies in the Systems (Ti, V)₂O₃†

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A model for the Ti, V₂O₃ electronic *d* levels is proposed and shown to account satisfactorily for observed anomalous low-temperature specific heats in the system. In the (Ti, V)₂O₃ systems, in particular, empty *V d* levels lie so far below the conduction band as to penetrate the host valence band a short way.

Sjöstrand and Keesom¹ have measured the specific heat of a number of samples of Ti₂O₃ doped with varying amounts of vanadium. In the temperature range from a few tenths of a degree Kelvin to 20 K, they have discovered a remarkable anomaly. In this range, the specific heat exceeds expected values by as much as 3 orders of magnitude. Furthermore, after an initial steep, linear rise, this excess specific heat levels off and becomes almost independent of temperature.

In a series of publications, Sjöstrand and Keesom¹⁻³ have offered a "one-dimensional" band structure characteristic of the pure host material as a model for the origin of the anomaly. The "one-dimensional" model fits the specific-heat data extremely well. A similar model had been used for describing anomalies in the V₃Si system by Labbé and Friedel.⁴ However, as has been

argued elsewhere,^{5,6} a one-dimensional band can only be found in a three-dimensional lattice as an approximation to an highly anisotropic three-dimensional band. The structural characteristics of V₃Si lead naturally to extreme anisotropy while those of Ti₂O₃ do not. The existence of one-dimensional bands in the Ti₂O₃ structure would thus be as anomalous and difficult to understand as the curious specific-heat behavior it has been invoked to explain. Also, such a model predicts corresponding anomalies and anisotropies in other phenomena such as transport where, however, they have not been observed.⁵ A final puzzle is that each V ion seems to contribute only 0.12 of the 3 degrees of freedom we would expect (or 0.4 of the single degree expected in one dimension).

We thus take the position that the success of the "one-dimensional" hypothesis, although strik-