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C.-M. Chan and M.A. Van Hove

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A Comparison of the Missing-Row Model and Several Newer Models for the Reconstructed Ir (110)-(1X2) Surface

by

C.-M. Chan
Corporate Technology
Raychem Corporation
300 Constitution Drive
Menlo Park, CA 94025

and

M. A. Van Hove
Materials and Molecular Research Division
Lawrence Berkeley Laboratory
and
Department of Chemistry
University of California
Berkeley, CA 94720

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Abstract The structure of reconstructed Ir(110)-(1X2) is reanalyzed by Low-Energy Electron Diffraction. In addition to wider variations of the missing-row model, the Bonzel-Ferrer (sawtooth) model and related structures are examined. The missing-row model remains the favorite, virtually unchanged in all respects from an earlier LEED study. But the sawtooth model cannot be excluded as a possible structure.

Much work has been performed on the structure of the (1X2) reconstructions of the clean Ir, Pt and Au(110) surfaces, which are believed to be mutually similar. Several models have been discussed, foremost of which is the missing-row model, cf. Figure 1. Also prominent is the "sawtooth" model of Bonzel and Ferrer (1), cf. Figure 2. Early LEED work on Ir(110) (2, 3) clearly favored the missing-row model over several other models, but did not consider the sawtooth model, which was proposed later. LEED analyses of the (1X2) reconstructions of Pt(110) (4, 5) and Au(110) (6, 7) were, however, inconclusive; some of these analyses included the sawtooth model (5, 7). The missing-row model has been clearly favored by a number of other techniques; namely, for Ir(110), Field Ion Microscopy (8), and for Au(110), X-ray diffraction (9), Scanning Tunneling Microscopy (10), High-Resolution Electron Microscopy (11) and High-Energy Ion Scattering (12). Atom diffraction done on Pt(110) cannot easily distinguish between the missing-row and the sawtooth models, but rules out many other models (13, 15). Total-energy calculations do strongly favor the missing-row model over the sawtooth model for Ir(110) (16), Pt(110) (16) and Au(110) (16, 17).

The theory-experiment agreement in the previous LEED study (2, 3) for Ir(110)-(1X2) was far superior to the case of Pt(110) (4, 5) and Au(110) (6, 7). Also, good theory-experiment agreement was obtained (18) for Ir(110)-c(2X2)O. Therefore, the Ir(110) surface presents the most favorable case for solving the structure by LEED. Since our previous work (2, 3) did not consider the sawtooth model or large relaxations within the missing-row model (large expansions are suggested by results on Au(110) (9, 11, 12)), we here extend the LEED study for Ir(110) to these structures. At the same time, we consider a few alternate models inspired by the sawtooth model; namely, the "hollow-on-facet" and "ridge" models, defined below.

In the missing-row model shown in Figure 1, we vary the two topmost layer spacings and the lateral position of the second-layer atoms (while maintaining two mirror planes perpendicular to the surface). In the sawtooth model shown by position A in Figure 2, the geometrical position of the top-layer atom is varied in two different schemes as indicated by A_1 and A_2 in Table 1. In the A_1-sawtooth model, the top-layer atom is moved perpendicularly to the (110) surface while remaining directly over a third-layer atom. In the A_2-sawtooth model, the top-layer atom is moved perpendicularly to the (111) facet over a hollow site formed by two second-layer atoms and one third-layer atom. The hollow-on-facet model, as indicated by position B in Figure 2, is similar to the A_2-sawtooth model, but uses a different hollow site on the (111) facets: the top-layer atom moves perpendicularly to the (111) facet over a hollow site formed by one second-layer atom and two third-layer atoms. In the ridge model, as indicated by

position C in Figure 2, the top-layer atom is located on a bridged site of the ridge. A detailed summary of the geometrical parameters used in the different models is presented in Table 1.

We have used the same set of experimental LEED I-V curves, theoretical methods and non-structural parameters as in our previous work (2, 3). However, this time, five R-factors and their average are used, which include the Zanazzi-Jona R-factor used previously and the Pendry R-factor. These are the R-factors ROS, R1, R2, RRZJ and RPE which were already applied in a number of LEED analyses (19). Our structural selection is based on minimizing the average over the five R-factors.

The best five R-factor averages for each model are summarized in Table 2. The missing-row model with a topmost interlayer spacing of 1.20 ± 0.10 Å and a bulk-like second layer (and an inner potential of 9 eV) is the best model among all those we have considered (this spacing corresponds to a 12 ± 5% contraction relative to the bulk interlayer spacing of 1.3585 Å). These optimum parameter values are nearly identical to our previous published results (2, 3). However, there remains considerable room for improvement. On the other hand, the sawtooth model of Bonzel and Ferrer performs nearly as well and thus we are not able to rule out this model. The Zanazzi-Jona, Pendry and 5-R-factor-average values are 0.30, 0.66 and 0.29 for our best missing-row model, and 0.32, 0.56 and 0.31 for our best sawtooth model, respectively. By contrast, the hollow-on-facet and ridge models are much worse. Averaged R-factor contour plots are presented in Figures 3 and 4 for the missing-row and sawtooth models, respectively, to illustrate the sensitivity to the main structural parameters.

In conclusion, the missing-row model remains the most likely for Ir(110)-(1X2) based on LEED. But we cannot exclude the sawtooth model for Ir(110). Also, we see no evidence for a large top-layer expansion (~ 0.5Å) in the missing-row model for Ir(110), contrary to such conclusions for Au(110) obtained with other techniques (9, 11, 12). In addition, parallel displacement greater than 0.2 Å in the second layer is not observed.

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Table 1: Summary of the Geometrical Parameters Used in Different Models

Model*	Range of Geometrical Variables, Å	Increment in the Variables, Å
Missing-row	d_1 = 0.6585 to 1.9885	0.07
Missing-row with row pairing	d_1 = 0.8585 to 1.7585 d_2 = 0.8585 to 1.7585	0.1 0.1
	$\frac{\beta}{2}$ = 1.5212 to 2.7212	0.2
A_1 Sawtooth	d_1 = 1.1485 to 1.4985 d_2 = 1.0788 to 1.6385	0.07 0.07
A_2 Sawtooth	ℓ = 2.3094 to 3.1925 d_2 = 1.0788 to 1.6385	0.07 0.07
B Hollow-on-Facet	ℓ = 2.3094 to 3.1925	0.07
C Ridge	d_1 = 0.6585 to 1.9885	0.07

A_1 = The top-layer atom is sitting on top of a third-layer atom.

A_2 = The top-layer atom is sitting in a hollow site perpendicularly to the (111) facet formed by two second-layer atoms and one third-layer atom.

B = The top-layer atom is sitting in a hollow site perpendicularly to the (111) facet formed by one second-layer atom and two third-layer atoms.

C = The top-layer atom is sitting on the short-bridged site of the ridge.

d_1 = The spacing between the first and second layers of atoms.

d_2 = The spacing between the second and third layers of atoms.

β = The change in inter-row spacing in the second layer of atoms, referred to the bulk.

ℓ = The bond length between atoms in the top layer and atoms in the nearest (111) facet.

*(See Figures 1 and 2)

Table 2: A Summary of the R-Factor Analysis

Model	Geometrical Parameters, Å	V_o, eV	Averaged R-Factor
Missing-row	d_1 = 1.2007	9	0.2829
Missing-row with row pairing	d_1 = 1.1772 d_2 = 1.3585 $\frac{\beta}{2}$ = 1.9212	10	0.2872 (see Figure 3)
A_1 Sawtooth	d_1 = 1.1485 d_2 = 1.4285	10	0.3125
A_2 Sawtooth	d_1 = 1.1505 y = 0.0000 z = 1.7740 d_2 = 1.4285	10	0.3069 (see Figure 4)
B Hollow-on-Facet	d_1 = 1.1060 y = 0.0000 z = 2.7033	4	0.3768
C Ridge	d_1 = 1.4285	6	0.3920

FIGURE CAPTIONS

Figure 1 (a), (b) Top and side views of a hard-sphere representation of the missing-row model.

(c) The geometrical parameters used in the missing-row model where a = 3.84Å is the bulk-like spacing between rows of atoms in the [001] crystallographic direction.

Figure 2 (a) Top view of a hard-sphere representation of several models. Site A is the sawtooth model; Site B is the hollow-on-facet model; and Site C is the ridged model.

(b) The corresponding side view of (a).

Figure 3 Contour plot of the average of five R-factors as a function of d_1 and d_2 for the missing-row model with β = 3.8424Å.

Figure 4 Contour plot of the average of five R-factors as a function of ℓ and d_2 for the A_2-sawtooth model.

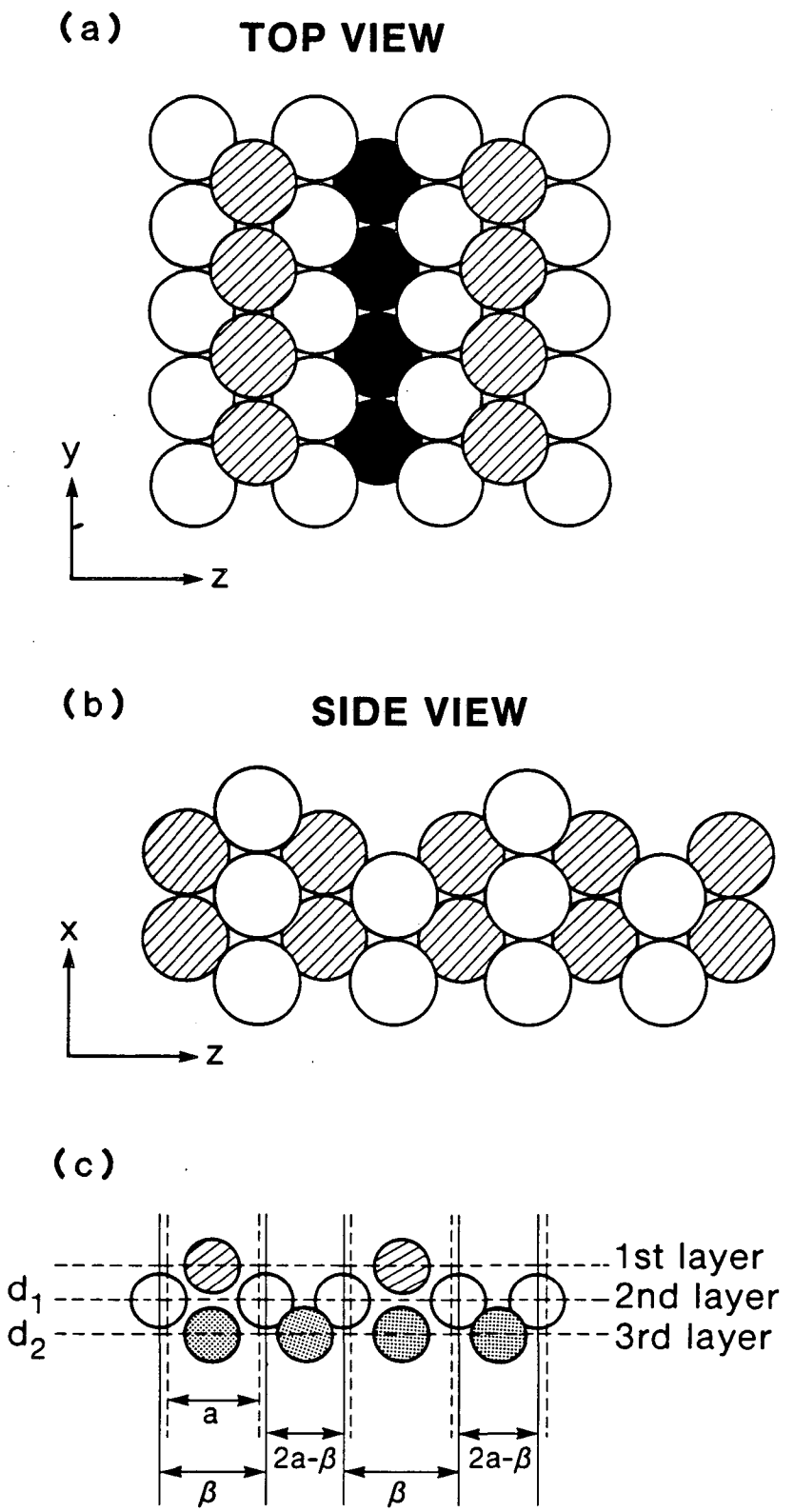
(a)
TOP VIEW
y
z
(b)
SIDE VIEW
x
z
(c)
1st layer
2nd layer
3rd layer
d_1
d_2
a
2a-β
2a-β
β
β

Figure 1

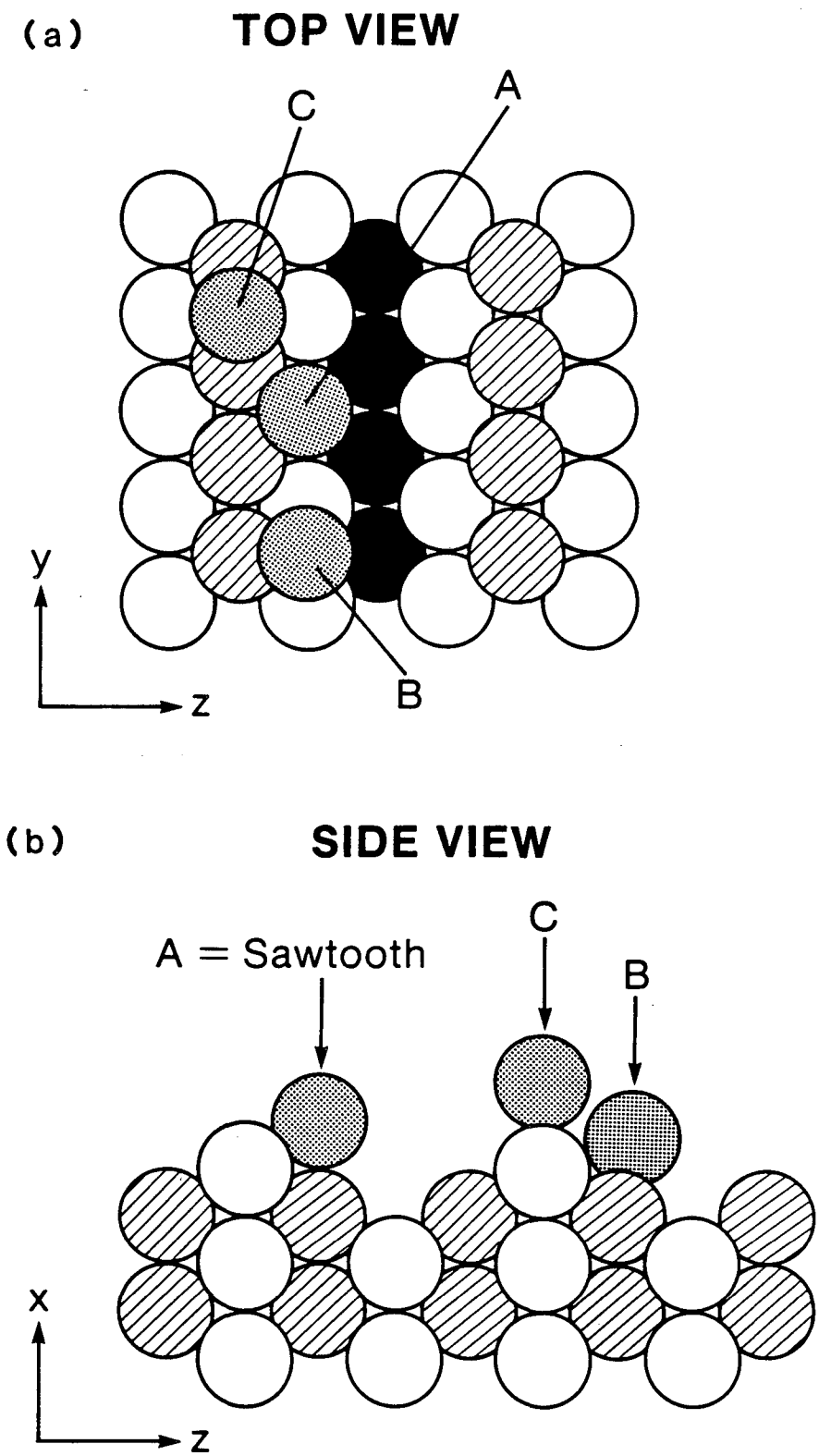

Figure 2

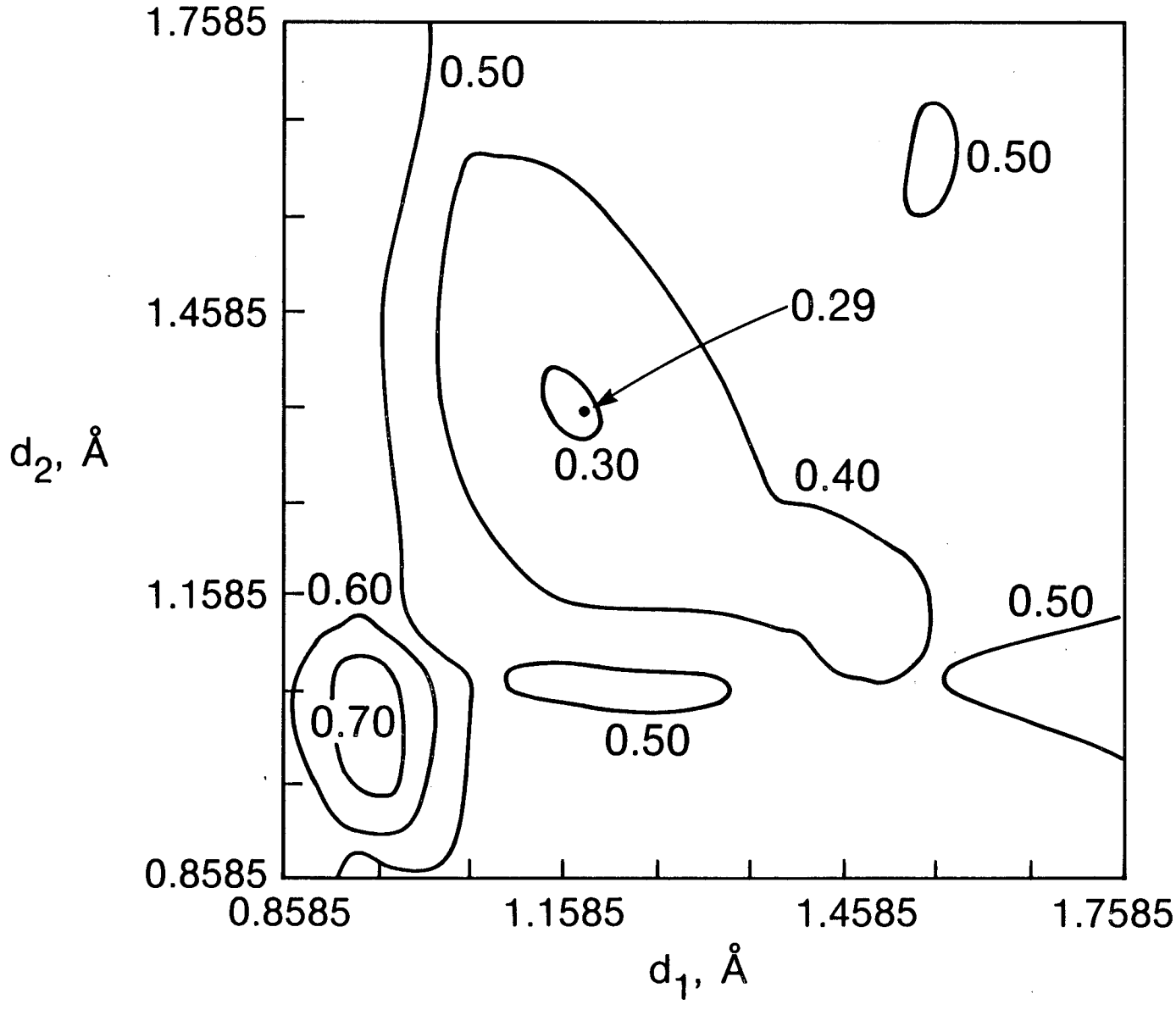
1.7585
1.4585
1.1585
0.8585
d_2, Å
0.8585
1.1585
1.4585
1.7585
d_1, Å
0.50
0.50
0.29
0.30
0.40
0.60
0.50
0.70
0.50

Figure 3

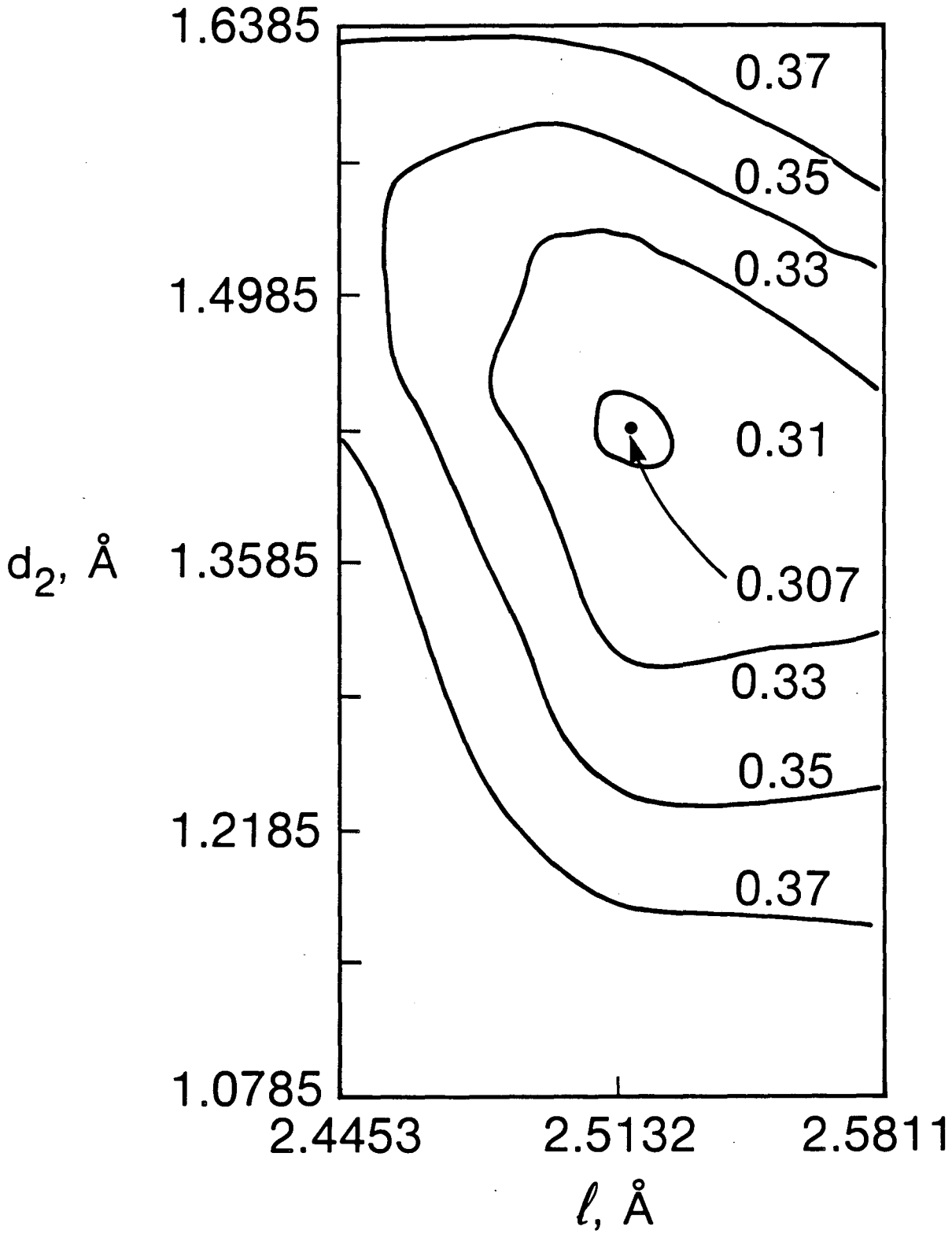
1.6385
1.4985
1.3585
1.2185
1.0785
d_2, Å
0.37
0.35
0.33
0.31
0.307
0.33
0.35
0.37
2.4453
2.5132
2.5811
ℓ, Å

Figure 4

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