PNL-SA-18242
CONF-901035--12

PNL-SA--18242

DE91 002811

A LEED STUDY OF THE MgO(001) SURFACE STRUCTURE

D. L. Blanchard
D. L. Lessor
J. P. LaFemina
D. R. Baker
W. K. Ford
T. Guo

October 1990

Presented at the
37th Annual AVS Symposium and
Topical Conference
Toronto,Canada
October 8-12, 1990

Work Supported by
the U. S. Department of Energy
under Contract DE-AC06-76RLO 1830

MASTER

Pacific Northwedt Laboratory
Richland, Washington 99352

A LEED STUDY OF THE MgO(001) SURFACE STRUCTURE

D.L. Blanchard, D.L. Lessor, J.P.LaFemina, D.R. Baer

Molecular Science Research Center

Pacific Northwest Laboratory

Richland, Washington 99352

W.K. Ford[a], T. Guo[b]

Advanced Materials Center and Department of Physics

Montana State University

Bozeman, Montana 59717

LEED beam intensities were measured from the freshly cleaved (in UHV) MgO(001) surface using beam energy modulation to avoid electrical charging. Dynamic LEED analysis of the data indicates: (1) an interlayer relaxation of (1±2)% and a rumple of the first layer ions of (5±2.5)%; (2) a new attenuation model containing no adjustable parameters gives fits to the data that are comparable to those using a constant V_i; (3) a weak dependence of the optimum rumpling on the energy range of the data used. The structure determined in this study is compared to others reported in the literature for this surface, and the effects of lattice vibrations, attenuation length and number of surface layers treated exactly are considered.

I. Introduction

The structure of the clean (001) face of MgO has been the subject of more than a few investigations over the past two decades[1-18]. This interest is due in part to its technological use as a substrate for thin film growth and as an important refractory material. The initial interest in this surface, however, was motivated by predictions that the anions and cations undergo different relaxations due to their differing polarizabilities. Theoretical predictions of the size and even existence of such a differential relaxation, or rumple, (defined in Fig. 1 as $\Delta_{1\perp}$), has been the subject of some debate[1-6]. Predicted values vary from 0%[1] to 2.4%[4] of the bulk Mg-O distance. (In all cases the anions move into the vacuum relative to the cations.) The spread in the predicted relaxation of the surface, (the change in spacing between the first two layers $\delta d_{12\perp}$ - see Fig. 1), is even larger, ranging from 11.2%[3] to 0.3%[4]. The experimentally determined values for these parameters are also fairly scattered as will be discussed later.

Due to this discrepancy in the surface geometry reported in the various studies to date (both theoretical and experimental), one of the goals of this paper is to attempt to clarify the true nature of the rearrangements of the atoms at the surface. Our interest is also motivated by the desire to extend surface structure analysis to environmentally important oxide systems. Work on this surface will, it is hoped, provide insight into techniques necessary for the study of more complicated surfaces of compound solids that are more highly insulating and less stable to electron beams, such as carbonates and aluminosilicates.

We present here a new set of LEED IV data from this insulator surface acquired using a beam modulated in energy over time at normal incidence. This was analysed using a multiple scattering treatment. Unlike previous analyses of this surface, we have used Hara exchange in the phase shift calculation, several energy ranges for theory/experiment comparison, and have incorporated a model recently proposed[19] for the electron inelastic mean free path (IMFP) in the analysis to assess its use for these compounds and in LEED analysis generally.

II. Experimental

The experimental system consists of a UHV chamber equipped with standard LEED optics, a sample cleaver and two evaporation sources. A large single crystal of MgO was cleaved to produce a roughly 5 mm X 5 mm X 15 mm bar. This was mounted on a sample holder which allowed heating of the crystal to 750 K and cooling to 165 K, as described previously[20]. The bar could be cleaved several times to expose fresh (001) surfaces.

MgO has a very wide band gap of about 7.8 eV, and so it charges quickly at low beam energies. In order to get reliable data below 140 eV incident energy, it was necessary to pulse the beam to an energy at which the secondary electron emission current exceeds the incident electron beam current. It was found that a 450 eV pulse for 1/3 s discharged the surface long enough to allow data acquisition for roughly 2/3 s before the surface charged up again. Therefore the incident electron beam was modulated between 450 eV and the energy of interest. It was also observed that the surface was slower to charge up at lower temperatures. For this reason, and to reduce effects due to lattice vibrations, all data were taken at a sample temperature of 165 K.

The surface did not appear to degrade significantly under the electron beam. Different areas on the crystal and different cleaves gave essentially identical IV curves.

The LEED system has been described in detail elsewhere[20]. Data was acquired from the reverse view phosphor screen with a high resolution CCD based video camera linked to an Apple Macintosh II microcomputer. The LEED flange (electron gun and optics) could be adjusted so that the beam/optics axis was within .5° of the surface normal as described previously[20]. All scans were taken at normal incidence. The diffraction spots were tracked over the energy range with data taken at 2 eV intervals. The background was subtracted from each beam at each energy. In most cases, eight beams could be tracked while cycling through the desired energies in a run. Runs were generally repeated 10 times and then averaged. The normal beam incidence geometry combined with the four-fold symmetric MgO unit cell gives rise to four fold symmetry in the LEED pattern. This allowed further averaging of equivalent beams. Differences in the curves at both averaging steps were within the noise level. The {10}, {11}, {20}, {21}, {22} and {30} families of beams were tracked, and all beams were averaged as described to produce the six inequivalent curves. All were subsequently used in the analysis. Before comparison to calculated curves, the data were normalized to the incident beam current, which varies with beam energy in the instrument used[20].

III. Method of LEED Analysis

The method of Laramore and Duke[21] was used for calculation of IV curves for comparison to the experimental LEED IV data. This treatment has proven succesful in atomic geometry determination of semiconductor surfaces, both

clean and with epitaxical overlayers[22]. In this approximate multiple scattering model, scattering from a species in the lattice is represented by energy dependent phase shifts for each order of spherical wavelet scattered. Intensities in the diffracted beams are calculated from phase shifts, the near surface geometry, and non-structural parameters such as those characterizing inelastic processes or the effective crystal potential well depth V_o (the inner potential). Scattering amplitudes associated with the uppermost few layers are evaluated exactly, as are those of the individual layers below. Twelve atomic layers and seven phase shifts (for orbital angular momentum eigenstates 0 through 6) were used in the present study. Four layers were treated exactly for survey calculations, followed by refinements using 6 layers exact. The figure of merit used in this work is the X-ray reliability factor, R_X[23].

The electron - ion-core interaction is described by a one-electron muffin-tin potential formed from a superposition of atomic charge densities. Muffin-tin radii are determined at the location of equal potential from atoms separated by the bulk Mg-O distance. The well depth outside the muffin-tin spheres measured from the vacuum level is the empirical inner potential parameter V_o. Phase shifts from a muffin-tin potential of each species are calculated from its charge density and potential in a Schrödinger equation solution using Hara exchange, as appropriate for electrons well above the Fermi level of the electron gas. Because the structures determined with this method are insensitive to the assumed ionic charges and their associated radii in the energy ranges covered in this study[8,13], the scattering species were treated as neutral atoms. Lattice vibrations were taken into account by renormalizing the electron - ion-core vertex with the use of a Debye-Waller factor[24,25].

Inelastic processes are characterized by an imaginary part of the wave vector which can be related to an imaginary optical potential, V_i, in the crystal interior. The energy dependance of the inelastic processes in LEED experiments has frequently been accounted for by using either a constant attenuation length, λ, or a constant V_i, which implies an attenuation length proportional to the square root of the energy. Either λ or V_i is usually taken as a parameter for optimization, but in this work we consider also an expression developed by Tenuma, Powell and Penn[19] to give λ and hence also V_i as a function of energy. These authors have found that the inelastic mean free path of electrons in a number of different materials is well described over a wide range of incident electron energies (50-2000eV) by a modification of the Bethe equation. Their empirical relationship depends only on the incident energy; the number of valence electrons per atom, molecule or formula unit; the atomic, molecular or formula weight; the bulk density; and the band gap energy. Figure 2 shows a comparison of the IMFP for the two different treatments. It can be seen that the TPP expression predicts less attenuation for energies above 50eV than that predicted by a constant V_i of 5eV. The relevance of this difference is addressed in section V.

IV. Results

Figure 3 shows a comparison between the experimental and calculated {01} and {11} IV curves. As mentioned previously, the experimental curves are averages of symmetrically equivalent beams. The theoretical curves were calculated with the top 6 layers treated exactly for a structure with a V_i of 5eV, an outward relaxation of the top layer of ions by 1% of the normal Mg-O bond distance ($\delta d_{12\perp}/d_{nn}=.01$) and a differential relaxation (the shear or rumple) of the O anions outward (relative to the Mg ions) of 5% of this bond distance

($\Delta_{1\perp}/d_{nn}$=.05). This fit gave an R_x value of approximately 0.10 over an energy range of 70eV to 340eV and is based on the final optimized variables. The analysis actually began with a preliminary R-factor search over the two structural parameters with 4 layers treated exactly and a guessed imaginary potential V_i=5eV. This led to tentative optimum values for the shear and relaxation, and to an approximate value for the inner potential V_o=19eV.

The optimum parameters from this preliminary search were then used to optimize V_i, which was then used in another search over the structural parameters. Throughout these iterations the optimum values of the parameters changed by <20%. The region near the last R_x minimum was then searched using the TPP inelastic mean free path as a basis for the attenuation length and the imaginary part of the propagation vectors, instead of a constant V_i. The R_x values found in this search were inferior to (larger than) those using V_i=6eV. When the number of layers treated exactly was increased from 4 to 6 the R_x values using the TPP model were much improved, and the optimum in the imaginary potential model declined from 6eV to 5eV. The optimum value for the mean square displacement of the atoms due to lattice vibrations, $\langle u^2 \rangle$, was zero for the constant V_i models, and near or at zero using the TPP model.

Finally, the structural parameters $\delta d_{12\perp}$ and $\Delta_{1\perp}$ were searched again, but with 6 layers treated exactly and for the two attenuation models, V_i=5eV and TPP. The R_x values using the TPP model showed dramatic improvement over the 4 layer case and became comparable with those found using the constant optical potential, which also were somewhat improved. This suggests that the use of longer attenuation lengths in calculations gave greater accuracy but only if multiple scattering was more accurately computed. The results of these searches, which range over all physically reasonable structures, are shown in

Fig. 4 for two different upper energy cutoffs: 280eV and 340eV. No other minima were found when other structures were tested. This is the first time the TPP model has been applied to a LEED IV analysis and considering that it contains no arbitrary parameters the agreement is very good.

V. Discussion

The results in the optimization sequence outlined above show the coupling of attenuation model and number of layers treated exactly in optimally fitting the experimental data. If too few layers are given an exact multiple scattering treatment, then the favored attenuation models will be ones having higher levels of attenuation from inelastic processes. Switching from 4 to 6 layers exact reduced the optimum V_i from 6 to 5 eV, and caused the TPP R_x values to go from very poor to nearly as good as the values with optimum V_i. Apparently the loss of interference details due to an inadequate treatement of multiple scattering may be compensated for, in part, by greater attenuation, and this is reflected in the optimization procedure.

Attenuation from inelastic processes and the effects of lattice vibrations also have similar effects in the computed IV curves and the R_x values. Lattice vibrations remove intensity from the diffraction peaks and redistribute it somewhat more evenly throughout the Brillouin zone. The overall effect is similar to that resulting from inelastic processes. All else being equal, lattice vibrations induce the greatest effects at the higher energy ranges of LEED, so the use of an assumed attenuation length that rises more slowly with increasing energy than the true one can be partially compensated for by an underestimate of lattice vibrations. This explains the preference for a rigid lattice over a non-zero $\langle u^2 \rangle$ when using the V_i=6eV

attenuation model. The latter overstates inelastic processes, which are partially accounted for by a reduction in the optimum amount of lattice vibrations. Because of this ambiguity, lattice vibrations are not well determined by data taken at a single temperature.

To obtain a measure of uncertainties, a comparison was made between optimum values of the two structural parameters with different energy ranges and with two different models for the inelastic processes leading to elastic beam attenuation. Energy ranges used were 70eV - 280eV, 70eV - 340eV, 100eV - 280eV, and 100eV - 340eV. The attenuation models were constant V_i=5eV and the TPP inelastic mean free path model. Results are shown in Table I. It is seen that choices of energy range that increase the weighting of higher energies, either by extending the energy range upward or by deleting from the low energy end of the energy range, tend to favor structural parameters closer to a truncated bulk. This might be a consequence of the loss of surface sensitivity in going to higher energies. Clearly a preferred technique for studies of extremely resistive materials prone to electrical charging is a low beam current one, i.e. digital LEED, which would obviate beam modulation to maintain specimen neutrality and permit use of lower energies. For the present study, the differences in optimized structure between the V_i=5eV and the TPP attenuation models are small. The four energy ranges shown for the V_i=5eV attenuation give $\delta d_{12\perp}/d_{nn}=(0.65\pm0.7)\%$ and $\Delta_{1\perp}/d_{nn}=(5.0\pm0.7)\%$. The four energy ranges shown for TPP attenuation give $\delta d_{12\perp}/d_{nn}=(0.9\pm0.6)\%$ and $\Delta_{1\perp}/d_{nn}=(5.1\pm0.6)\%$. Taken together these give $\delta d_{12\perp}/d_{nn}=(0.8\pm0.6)\%$ and $\Delta_{1\perp}/d_{nn}=(5.0\pm0.7)\%$. The stated standard deviations include only effects from energy range and attenuation model, and hence inherently understate the uncertainty.

A second estimate of the uncertainties in the determined structural parameters can be made from an estimate of the uncertainty in R_x. This was obtained by Ford et al[26] by comparing R_x values calculated for different IV scans of identical diffraction beams on GaAs(110), for both simple rescans and new cleavages. This was the same apparatus used in this study, and despite differences, Ford et al's estimated uncertainty of 0.01 in R_x for a fixed energy range is a reasonable estimate here. The regions enclosed by contours of R_x which are 0.01 larger than the minima for the two energy ranges in Fig. 4 show considerable overlap, with the overlap region centered at [$\delta d_{12\perp}/d_{nn}$ = (1±2)%, $\Delta_{1\perp}/d_{nn}$ = (5±2.5)%]. We take this as the best estimate reconstruction from the present study.

Table II presents the results of experimental studies of the MgO(001) surface structure, including LEED, RHEED and impact collision ISS (ICISS). The results of this study agree qualitatively with most of the electron diffraction results in that we discern very little relaxation of the top layer. In addition, we concur with Welton-Cook and Berndt[13] in the identification of a rumple in the top layer of ions. The source of the discrepancy in the size of the rumple is unknown. The other two LEED studies, though in other respects very thorough and solid contributions, gave the possibility of rumpling only cursory consideration, and were not R factor assisted. The RHEED study by Maksym was not capabable of discerning a rumple due to the diffraction conditions of the experimental data, so this possibility was left open.

The rumple that we observe is closer to that reported by Gotoh et al[11] using RHEED Kikuchi lines to elucidate surface structure. These authors report that the surface rumples only after annealing at 300°C, however, and in this study the rumple is observed on the freshly cleaved surface. Urano et al[14] have

found that, whether freshly cleaved or annealed, the LEED IV curves for MgO(001) are essentially identical. Considering this observation, and the report of a rumple on the freshly cleaved surface (this study) as well as on the annealed surface (ref. 13) we must conclude that the surface is rumpled, and that this rumpling occurs immediately upon cleaveage.

The very large surface contraction of MgO(001) reported in the ICISS study[15] is difficult to reconcile with the electron diffraction results. The authors suggest that neutralization probability differences between anions and cations and between the 1st and 2nd layer may contribute to problems in the data analysis. For this reason, and because of the fairly recent development of the technique, we regard the ICISS results as very interesting, but are somewhat skeptical of their accuracy.

VI. Summary and Conclusions

LEED IV curves from the MgO(001) surface, prepared by cleavage in situ, were taken using beam modulation to control charging. An R-factor assisted analysis of the data was performed using an approximate multiple scattering treatment to calculate the comparison curves. Two different models were used to describe the attenuation of electrons in the solid. A constant imaginary potential, V_i, is more succesful than the attenuation model proposed by Tenuma, Powell and Penn[19] when only 4 layers at the surface were treated exactly. For 6 layers, however, the two models give very comparable results, and the agreement with the experimental data is quite good. Comparison of calculated to experimental curves was considered over 4 energy ranges for the two different attenuation models. Agreement is good, giving a relaxation of

(1±2)% and a rumple of (5±2.5)%. Thus we conclude that the surface is rumpled when freshly cleaved, as well as after annealing[13].

Acknowledgements

The authors wish to thank Lambert Bates for his donation of MgO single crystals, and Mark Engelhard for technical assistance in some of the crystal preparation and characterization. This work was supported by the US Department of Energy through contract DE-AC06-76RLO 1830 with Battelle Memorial Institute.

a) Present address: Intel Corporation, 5200 NE Elam Young Pkwy, M/S AL3-15, Hilisboro, OR 97124.

b) Present address: Gould AMI Semiconductors, Research and Development, 2300 Buckskin Rd., Pocatello, ID 83201.

1) M.R. Welton-Cook and M. Prutton, Surf. Sci. 74, 276 (1978).

2) A.J. Martin and H. Bilz, Phys. Rev. B19, 6593 (1979).

3) G.V. Lewis and C.R.A. Catlow, J. Phys. C18, 1149 (1985).

4) F.W. deWette, W. Kress, and U. Schröder, Phys. Rev. B32, 4143 (1985).

5) V.C. Lee and H.S. Wong, J. Phys. Soc. Jpn. 45, 895 (1985).

6) J.P. LaFemina and C.B. Duke, JVST, in review.

7) K.O. Legg, M. Prutton, and C. Kinniburgh, J. Phys. C 7, 4236 (1974).

8) C.G. Kinniburgh, J. Phys. C 8, 2382 (1975).

9) ibid., J. Phys. C 9, 2695 (1976).

10) Y. Murata, S. Murakami, H. Namba, T. Gotoh, and K. Kinosita, in: *Proc. 7th Intern. Vac. Congr. & 3rd Intern. Conf. Solid Surfaces*, Vienna, 1977, p. 2439.

11) T. Gotoh, S. Murakami, K. Kinosita, and Y. Murata, J. Phys. Soc. Japan 50, 2063 (1981).

12) P.A. Maksym, Surf. Sci., 149, 157 (1985).

13) M.R. Welton-Cook and W. Berndt, J. Phys. C 15, 5691 (1982).

14) T. Urano, T. Kanaji, and M. Kaburagi, Surf. Sci. 134, 109 (1983).

15) H. Nakamatsu, A. Sudo, and S. Kawai, Surf. Sci. 194, 265 (1988).

16) C. Schwartz, M. Karimi, and G. Vidali, Phys. Rev. B 39, 11131 (1989).

17) D.R. Jung, M. Mahgerefteh, and D. R. Frankl, Phys. Rev. B 39, 11164 (1989).

18) K.H. Rieder, Surf. Sci. 118, 57 (1982).

19) S. Tanuma, C.J. Powell and D.R. Penn, J. Vac. Sci. Tech. A 8, 2213 (1990)

20) T. Guo, R.E. Atkinson, and W.K. Ford, Rev. Sci. Inst. 61, 968 (1990).

21) G.E. Laramore and C.B. Duke, Phys. Rev. B2, 4783 (1970).

22) C.B. Duke in Surface Properties of Electronic Materials, ed. D.A. King and K.P. Woodruff, Chap. 3 (Elsevier, 1988) and references therein.

23) E. Zanazzi and F. Jona, Surf. Sci. 62, 61 (1977).

24) C.B. Duke and G.E. Laramore, Phys. Rev. B2, 4765 (1970).

25) C.B. Duke, N.O. Lipari and V. Landman, Phys. Rev. B8, 2454 (1973).

26) W.K. Ford, T. Guo, D.L. Lessor and C.B. Duke, Phys. Rev. B, in review.

Table I Optimum structure for MgO(001) determined from LEED analysis as a function of attenuation model and energy range.

Attenuation Model	Energy Range (eV)	$\delta d_{12\perp}/d_{nn}$ (%)	$\Delta_{1\perp}/d_{nn}$ (%)	R_x
V_i=5eV	70 - 280	1.44	5.66	0.092
	70 - 340	0.26	5.36	0.099
	100 - 280	0.99	4.41	0.048
	100 - 340	-0.09	4.39	0.062
Tanuma, Powell	70 - 280	1.57	5.54	0.098
and Penn	70 - 340	0.60	5.58	0.107
	100 - 280	1.26	4.49	0.070
	100 - 340	0.20	4.77	0.083

Table II Results of various experimental studies on the surface structure of MgO(001). The relaxation, $\delta d_{12\perp}/d_{nn}$, and shear, $\Delta_{1\perp}/d_{nn}$, follow from definitions in Fig. 1. Positive values of the relaxation indicate an expansion of ions into the vacuum. Positive values of the shear indicate an outward movement of the anions relative to the cations.

Reference	$\delta d_{12\perp}/d_{nn}$ (%)	$\Delta_{1\perp}/d_{nn}$ (%)	Method
8	$<\pm 3$	NR	LEED
13	$0\pm .75$	2 ± 2	LEED
14	0 to 2.5	NR	LEED
This study	1 ± 2	5 ± 2.5	LEED
11	NR	6	RHEED
12	<3	NR	RHEED
15	-15 ± 3	$.3\pm .9$	ICISS

NR = not reported

Figure Captions

Figure 1 - Schematic diagram of the surface geometry and definition of the structural parameters for MgO(001). A differential relaxation or rumple, $\Delta_{1\perp}$, of the first layer ions is depicted. Note that the unperturbed interlayer spacing, $d_{12\perp}$, is equal to the nearest neighbor distance, d_{nn}.

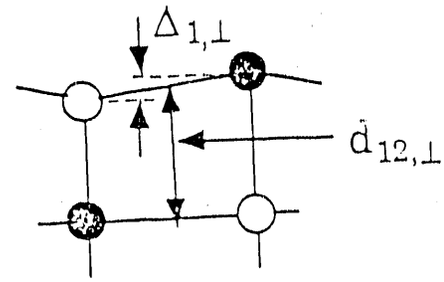
Figure 2 - Comparison of the inelastic mean free path in MgO as a function of energy for the attenuation model of Tenuma, Powell and Penn (TPP) and that of a constant imaginary potential of 5eV.

Figure 3 - Comparison of the measured and calculated IV curves for the averaged {10} and {11} beams. The solid lines are the computed intensities for MgO(001) surface with a 5% shear and a 1% relaxation.

Figure 4 - Contour plots of R_x in ($\delta d_{12\perp}/d_{nn}$, $\Delta_{1\perp}/d_{nn}$) space for two different attenuation models and comparison over two energy ranges: a) V_i=5eV, 70eV - 280eV; b) V_i=5eV, 70eV - 340eV; c) TPP, 70eV - 280eV; d) TPP, 70eV - 340eV.

MgO (001)

(a) Side View



● O

○ Mg

(b) Top View

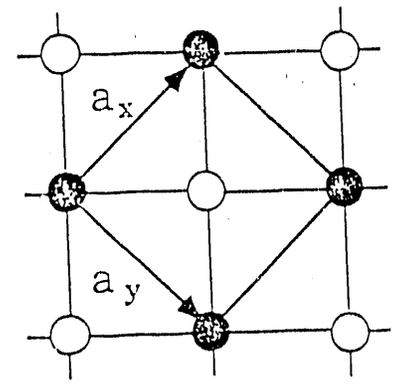


Fig. 1

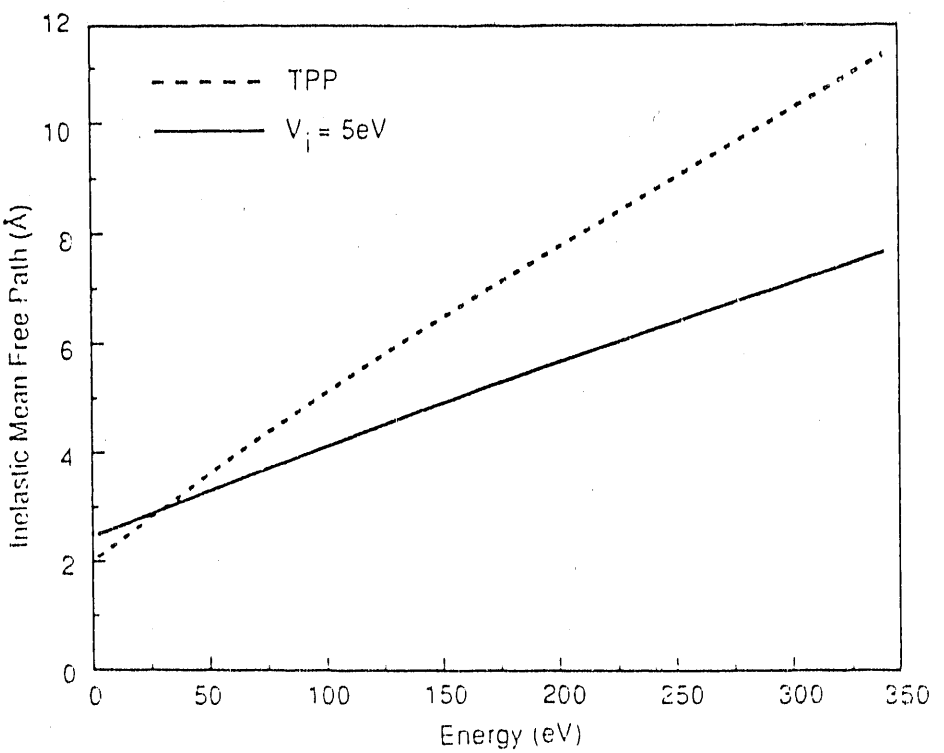

TPP
V_i = 5eV
Inelastic Mean Free Path (Å)
Energy (eV)
0
2
4
6
8
10
12
0
50
100
150
200
250
300
350

Fig. 2

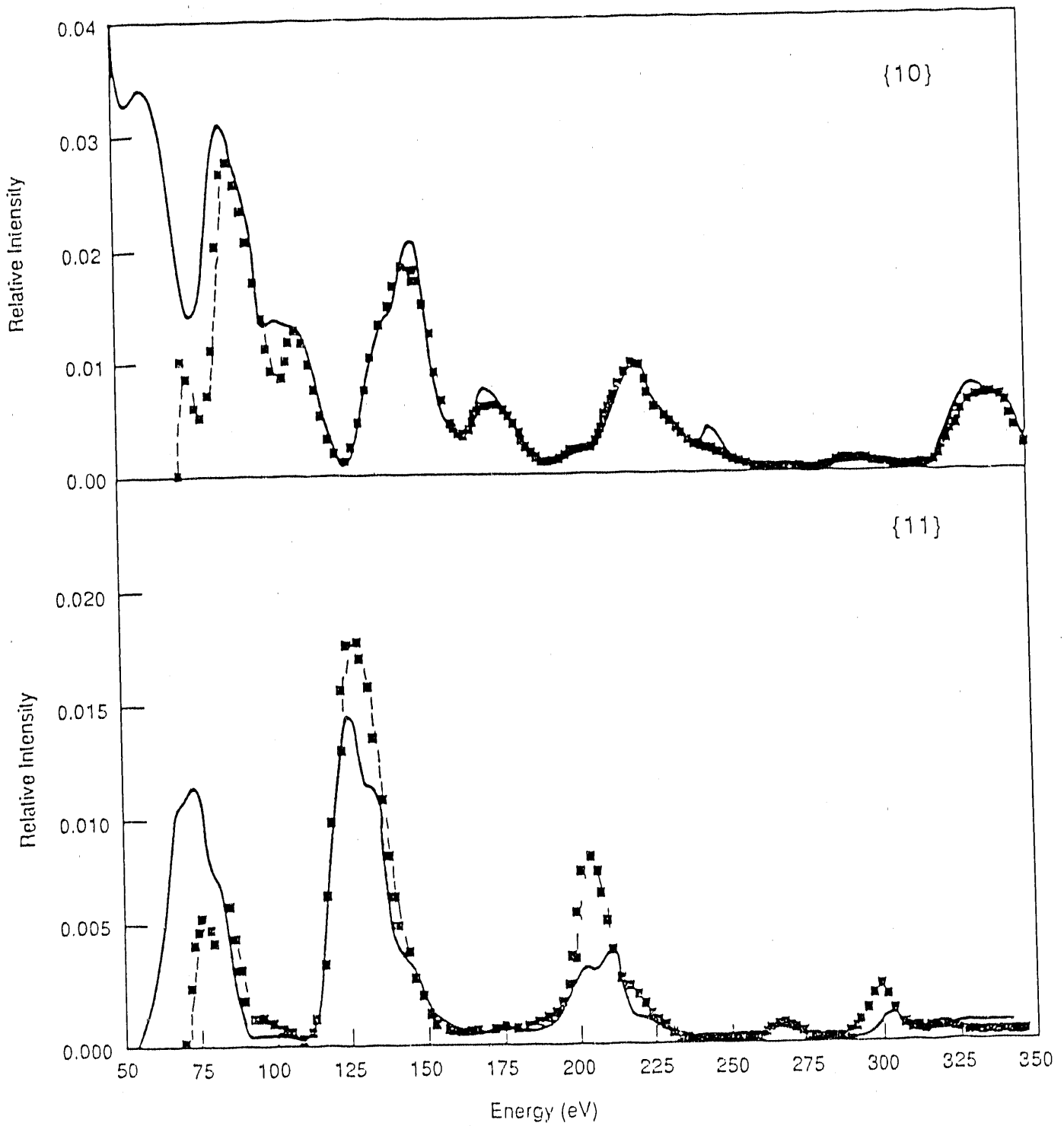
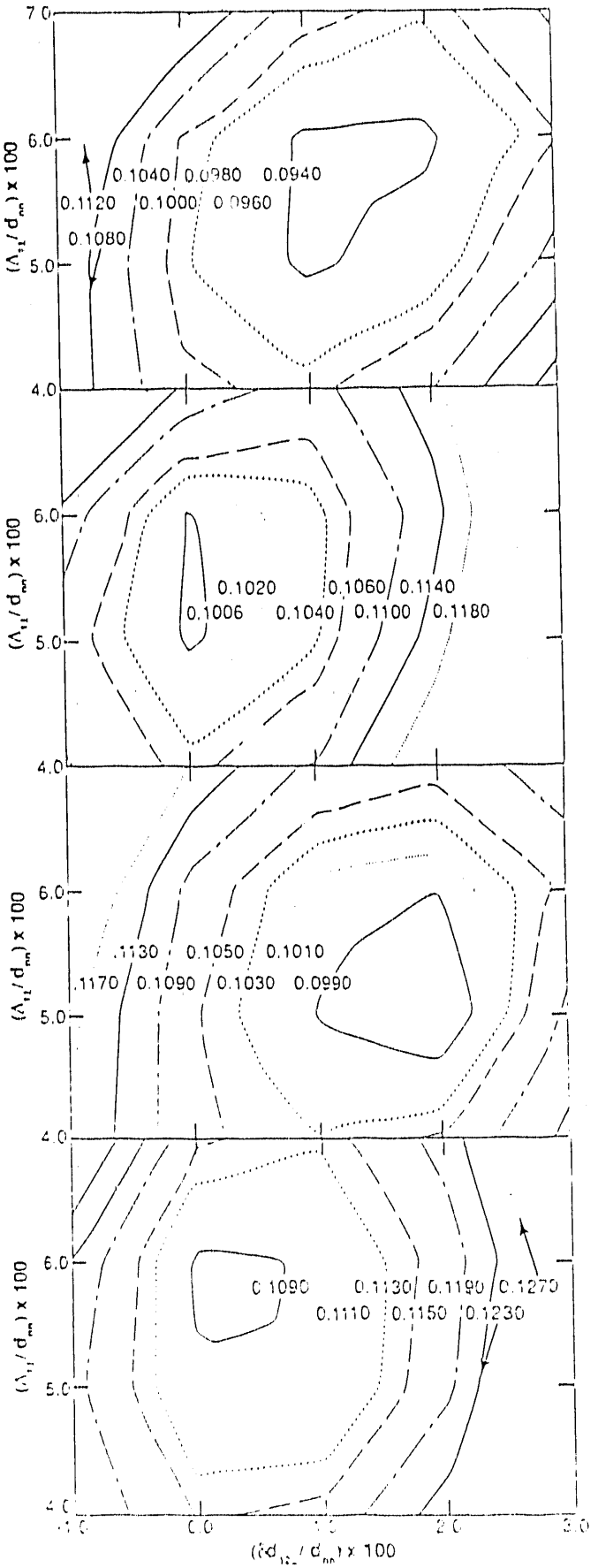

{10}
{11}
Relative Intensity
Relative Intensity
0.04
0.03
0.02
0.01
0.00
0.020
0.015
0.010
0.005
0.000
50
75
100
125
150
175
200
225
250
275
300
325
350
Energy (eV)

Fig. 3


7.0
6.0
5.0
4.0
$(\Lambda_{11}/d_{nn}) \times 100$
0.1040
0.0980
0.0940
0.1120
0.1000
0.0960
0.1080
0.1020
0.1060
0.1140
0.1006
0.1040
0.1100
0.1180
.1130
0.1050
0.1010
.1170
0.1090
0.1030
0.0990
0.1090
0.1130
0.1190
0.1270
0.1110
0.1150
0.1230
$(\delta d_{12}/d_{nn}) \times 100$

END

DATE FILMED

12/17/90