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MOLECULAR BEAM SCATTERING FROM CLEAN AND CARBON MONOXIDE COVERED PLATINUM (111) CRYSTAL SURFACES

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ABSTRACT

Scattering distributions of monatomic and diatomic gases from clean a CO covered Pt single crystal surfaces indicate efficient translational vibrational (T_B-V_S) energy transfer when the surface is CO covered. This efficient energy transfer is attributed to low frequency bending modes of the CO molecules on the surface which absorb the incident particle energy. The increased surface residence time resulting from this efficient energy transfer could be responsible for higher sticking probabilities of incident gases increased reaction rates for adsorption limited surface reactions.

INTRODUCTION

Atomic and molecular beams scattered from clean metal surfaces have shown poor energy accommodation with the scattering surface. The angular distribution of scattered H_2, O_2, N_2, NO, CO, and C_2H_2 [1,2] beams peak at or near the specular angle. Ammonia alone has shown the cosine like angular distribution upon scattering from the Pt(100) surface that would be expected if the incident molecules thermally equilibrated and then were reemitted from the surface. Although the surface temperatures T_S were generally greater in these experiments than the characteristic "beam temperatures," T_B, the temperature dependence of the angular distributions of the scattered beams do not explain the poor energy transfer between the incident molecules and the surface.

Siekhaus et al.[3] have monitored the velocity of scattered beams of many molecules directly, as a function of the surface temperature of graphite, and found poor energy accommodation above 400°K for all of the beam molecules. Even in the absence of determination of the scattered beam velocity, from the angular distribution studies it can be concluded that T_B-V_S or V_B-V_S energy transfer, i.e., energy transfer between translational or vibrational modes of the incident molecules and the phonon modes of the surface atoms of the solid is not an efficient process.

The nature of energy transfer changes radically, however, when molecules are scattered from a layer of adsorbed diatomic or polyatomic molecules, such as carbon monoxide or acetylene. In this paper we report on molecular beam scattering studies from these adsorbed layers on the platinum (111) crystal face. Invariably, atoms or diatomic molecules undergo complete thermal accommodation when scattered from

an adsorbed layer of carbon monoxide, as indicated by the cosine like angular distribution of the scattered beams. These studies indicate that energy exchange in the molecular beam-surface scattering process is predominantly via the T_B-V_S mechanism and that the low frequency localized bending modes of the absorbed molecules are likely to be responsible for the efficient energy transfer.

EXPERIMENTAL

The apparatus used in these scattering studies has been described very briefly previously.[4] For detailed information about the extensive modifications to the original apparatus,[5] see reference 6. Briefly, the apparatus is an ultra-high vacuum scattering chamber fitted with low energy electron diffraction (LEED) optics, Auger electron spectrometer (AES) and a rotatable mass spectrometer detector, attached to two diffusion pumped chambers for forming and modulating a molecular beam. The single crystal scattering surface can be chemically cleaned, ion sputtered, annealed, and characterized by LEED and AES in the scattering chamber. Pressures below 10^{-9} Torr allow the surface to be kept free of unwanted contaminants for times long enough to do the experimental measurements. The incident molecular beam is formed by effusion from an oven fitted with a multichannel capillary array, and modulated by a variable frequency mechanical chopper. Lock-in detection of the scattered beam is used to improve the signal to noise ratio. Angular distributions of the scattered molecules are determined by rotating the mass spectrometer detector around the scattering surface, in the plane of the incident beam and the surface normal. All of the experiments reported here used a modulation frequency of 160 Hz.

The scattering surface was the (111) plane of a Pt single crystal. The bulk rod (Materials Research Corporation) was oriented to within 0.5° of the (111) plane by back reflection of X-rays, and then a 1.5 mm slice was spark cut from the rod. The specimen was mechanically

polished with successively finer abrasives ending with 1μ diamond paste. The polished crystal was spotwelded to high purity Pt polycrystalline supports, etched in hot 50% aqua regia, and mounted on a Varian crystal manipulator in the scattering chamber. The crystal could be resistively heated and its temperature was determined by comparison with a similarly prepared crystal fitted with a Pt-Pt 10% Rh termocouple, or alternately by an infrared pyrometer.

After extensive ion bombardment, heat treatments, and oxygen cleaning the LEED pattern was that of the clean Pt(111) surface. An Auger spectrum of the surface exhibiting the clean LEED pattern showed large Pt peaks, no C or O peaks, and a small Ca peak. Once the clean crystal had been prepared, the clean surface was easily regenerated after CO adsorption, by heating to ~1100°K in 2×10^{-5} Torr O_2 for 1 hour and then pumping out the O_2 while the crystal was still hot.

The CO adsorbed layer was obtained by exposing the clean surface at 300°K to a pressure of 1.5×10^{-8} Torr CO for about 30 minutes. The resulting LEED pattern showed very high background and dim C(4×2) features[17] which were very sensitive to electron beam deterioration. All of the gases used in the beam, for cleaning, ion bombardment, and adsorption were Matheson research grade gases.

RESULTS AND DISCUSSION

Figure 1a shows the angular distribution of carbon monoxide and nitrogen molecular beams scattered from an adsorbed carbon monoxide layer. Both species have the same molecular weights but very different vibrational frequencies and rotational spectra. The figure clearly shows the cosine like angular distribution of the scattered beam, which implies complete energy accommodation of both gas molecules with the surface before reemission. Figure 1b shows the angular distribution of N_2 scattered from the clean platinum surface. Figures 2a and 2b show the angular distribution of hydrogen scattered from clean and carbon monoxide covered platinum (111) surfaces. Again, the scattered beam is highly specular from the clean metal surface, while cosine like from the CO covered crystal. Thus, it appears that the presence of an adsorbed layer of diatomic molecules greatly facilitates the energy accommodation of incident gas molecules.

The energy transfer responsible for this efficient accommodation can either be between the translational modes of the diatomic molecule in the beam and the vibrational modes of the carbon monoxide molecules adsorbed on the surface (T_B-V_S interaction), or vis the vibrational modes of the gas and the CO molecules on the surface (V_B-V_S interaction). Rotational energy transfer (R_B-V_S) is expected to be rapid and complete for both incident CO and N_2 molecules even with the clean platinum surfaces. Doll[7] calculates that the width of the angular distribution on scattering a rigid rotor as compared to atom scattering is markedly broader, in good agreement with experiments. Thus, it

appears that R_B-V_S energy transfer can readily take place within collision time from the clean metal surface. The exception appears to be that of hydrogen since large differences in the angular distribution of scattered H_2 and D_2 from clean surfaces have been detected.[8] Because of the larger mass of CO and N_2, the rotational energy states are closely spaced and readily available for energy transfer.

In order to learn which energy transfer process, T_B-V_S or V_B-V_S is responsible for the complete energy accommodation of the incident gas on the adsorbed layer we have scattered an argon atomic beam from the clean and carbon-monoxide covered Pt(111) surface. The results are shown in Fig. 3. Argon scatters specularly from the clean Pt(111) surface while, as Fig. 3 indicates, it exhibits a cosine like angular distribution when scattered from an adsorbed layer of carbon monoxide. This observation indicates that the T_B-V_S energy transfer process is responsible for the complete thermal accommodation of the argon atom and therefore the CO and N_2 molecules scattered from the CO covered platinum surface are most likely to be accommodated by the same mechanism in the presence of an adsorbed layer of carbon monoxide.

For the diatomic molecules, however, contribution of V_B-V_S energy transfer to the T_B-V_S process cannot be ruled out, although complete thermal accommodation of atoms has taken place in the absence of V_B-V_S energy exchange. Similar results, i.e. complete energy accommodation, have been obtained upon scattering acetylene (C_2H_2) from an adsorbed layer of C_2H_2.[1]

It appears that the vibration modes of the adsorbed molecules that are localized at the surface can readily absorb the kinetic energy of

the incident atom or molecule. These observations can readily be rationalized by assuming that on impact the molecules bend and absorb part of the impact energy by excitation of these low frequency bending modes. Once the incident atom or molecule loses enough kinetic energy that it can no longer desorb within a vibrational time, it becomes trapped on the surface long enough (between 10^{-6} and 10^{-3} seconds), for complete accommodation to occur.

It should be noted that the scattering experiments from an adsorbed CO layer were carried out at 300°K while from a clean platinum surface, at or above 500°K. This higher temperature was necessary to avoid contamination of the clean crystal surface by CO, which is ever present in the ultra high vacuum systems. In the absence of surface contamination, the angular distribution of scattered N_2, H_2 or Ar beams become more peaked with decreasing surface temperature. (See Fig. 4) Thus, the small temperature difference cannot account for the markedly different energy accommodation of the incident molecules, but it must be the result of the presence of the adsorbed CO which changes the nature of the molecular collision dynamics.

In many surface reactions the rate determining step is that of the adsorption of reactants. Our experiments indicate that the residence time of the incident molecules can be greatly increased by "contaminating" the surface with CO. Other diatomic or polyatomic molecules that provide the same efficient T_B-V_S channel for energy accommodation should be equally effective in increasing the residence time. Thus, the reaction probability should markedly increase in the presence of these impurities for reactions where reactant adsorption is the rate determining step.

For example, Bonzel and Ku[9] and Palmer et al.[10] report on the oxidation of CO on platinum crystal surfaces. It appears that the reaction proceeds readily with detectable rates on the Pt(100) surface. On the other hand other chemical reactions, H_2-D_2 exchange,[6] D_2-O_2 reaction etc.[11] could not be detected on clean (111) or (100) crystal faces of platinum. It would be of importance to investigate the effect of adsorbed gases with partial monolayer coverage on the surface reaction rates. These adsorbates may well "catalyze" surface reactions by increasing the residence time of the reactants on the surface. Of course, for certain other reactions adsorption of a partial monolayer of gas giving increased residence time could decrease the reaction rate by poisoning or blocking active sites. This appears to be the case for H_2-D_2 exchange on certain Pt surfaces.[6]

These results also indicate that the sticking probability of incident molecules should drastically depend on the state of cleanliness of the surface. In ultra high vacuum systems carbon monoxide is one of the most abundant contaminants. A partial monolayer coverage of adsorbed CO may change the sticking probability or rare gas atoms or of diatomic molecules by orders of magnitude. The controversy in the literature over the sticking probability of O_2 on Pt surfaces[12,13,14] could well be explained by this increase in residence time due to efficient energy transfer on surfaces with adsorbed CO layers.

It is of interest to explore the effect of the relative molecular weights of the incident molecules and the substrate atoms on the energy accommodation, since we have substituted heavy platinum atoms with light CO molecules as scatterers. West and Somorjai[15] and Merrill and Smith[16] have shown that graphitic carbon scatters He and O_2 specularly without

much energy accommodation.

It is important to separate the effect of atomic disorder from the effect of adsorbed CO on the angular distribution of the scattered molecules. Although the adsorbed CO layer is ordered as indicated by the diffraction pattern, it is likely that there are disordered areas in the adsorbate layer. Thus the scattering from the adsorbed layer may also show effects due to disorder. Clean stepped surfaces are ideally suited to explore the effect of disorder on the scattering without the presence of the adsorbed layer. We have compared the angular distribution of scattered H_2 from two clean stepped surfaces with the angular distribution from clean and CO covered Pt(111) surfaces. Figure 5 shows the results of this comparison. Scattering from the clean (111) surface is very strongly peaked. Scattering from the CO covered surface is cosine. Scattering from stepped surfaces is still quite specular, even though the surfaces contain roughly 10% (Pt-(s)[9(111)×(111)]) and 20% (Pt-(s)[5(111)×(111)] edge atoms. It would appear that the surface would have to be more than 50% disordered for the scattering distribution to become cosine from disorder or atomic roughness alone. In the case of the CO chemisorbed layer, the LEED pattern indicates that the surface is more highly ordered than this.

Smith and Merrill[16] have found that a D_2 beam scattered from a disordered carbon layer on top of platinum (111) was highly specular and did not show complete energy accommodation as it does on scattering from an adsorbed CO layer on platinum. Recent evidence from their laboratory[18] indicates that this specularity could be due to scattering

from the bare Pt surface after aggregation of the carbon layer. Therefore it appears that neither the change of molecular weight nor the change in the degree of order of the surface atoms is responsible for the marked change in the energy transfer with the incident gas atom or molecule. It appears that the localized vibrational modes provided by the adsorbed CO molecules, resulting in efficient T_B-V_S energy transfer, are responsible for the complete energy accommodations of the incident atomic or molecular beams.

ACKNOWLEDGMENTS

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Figure Captions

Figure 1. a) Scattering distribution of N_2 and CO from CO covered surface. b) Scattering distribution of N_2 and CO from clean surface.

Figure 2. a) Scattering distribution of H_2 from clean surface. b) Scattering distribution of H_2 from CO covered surface.

Figure 3. a) Scattering distribution of Ar from clean surface. b) Scattering distribution of Ar from CO covered surface.

Figure 4. Scattering distribution of Ar from clean surface at two different temperatures. Inset shows dependence of specular intensity on surface temperature.

Figure 5. Scattering distributions of H_2 from stepped Pt surfaces compared with clean and CO covered Pt(111).

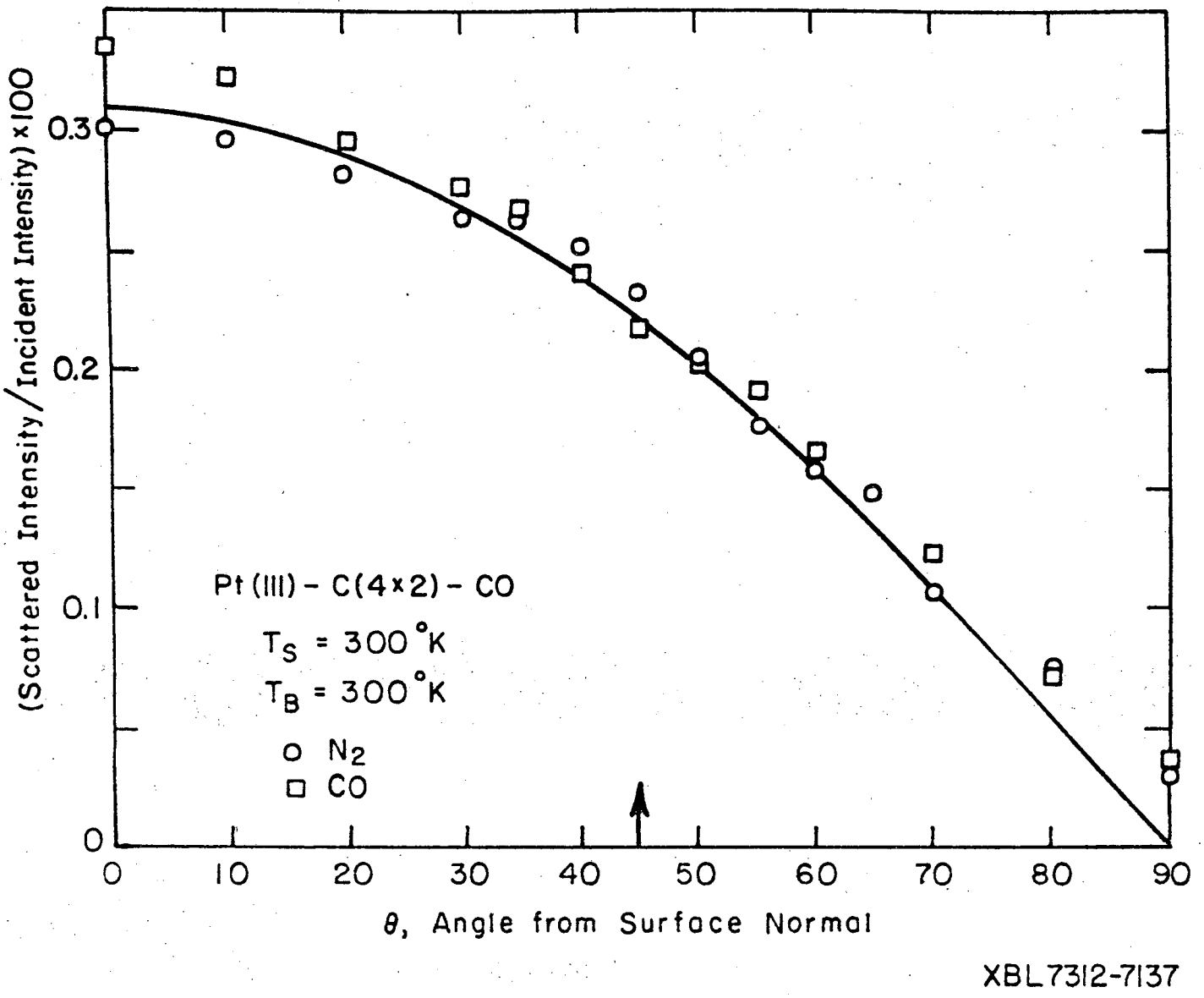
(Scattered Intensity / Incident Intensity) x100
0.3
0.2
0.1
0
Pt (III) - C(4x2) - CO
T_S = 300 °K
T_B = 300 °K
o N_2
□ CO
0
10
20
30
40
50
60
70
80
90
θ, Angle from Surface Normal
XBL7312-7137

Fig. 1a.

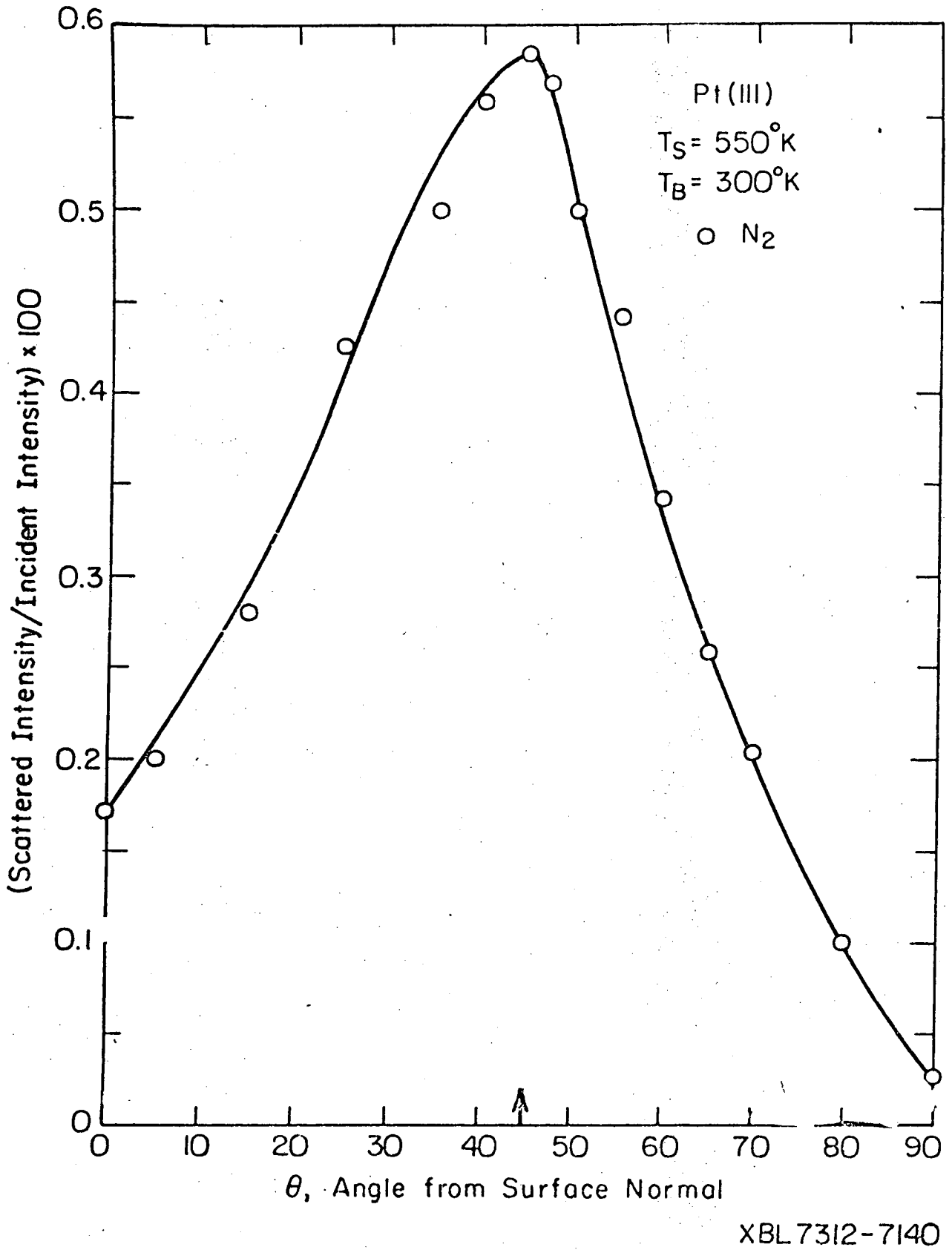
Pt(111)
T_S = 550°K
T_B = 300°K
o N_2
(Scattered Intensity/Incident Intensity) x 100
0.6
0.5
0.4
0.3
0.2
0.1
0
0
10
20
30
40
50
60
70
80
90
θ, Angle from Surface Normal
XBL7312-7140

Fig. 1b.

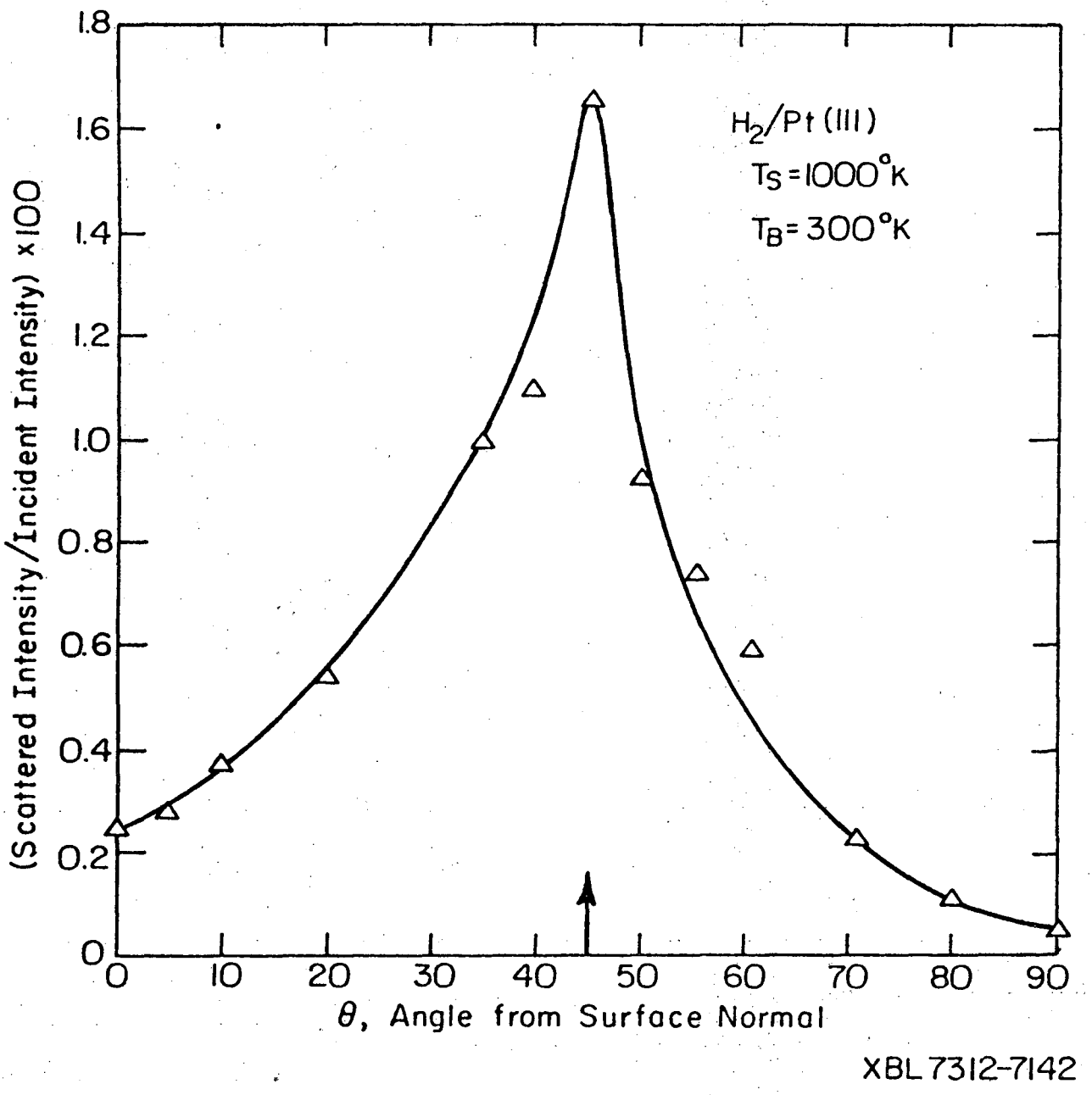
H2/Pt (111)
TS = 1000°K
TB = 300°K
(Scattered Intensity/Incident Intensity) x100
θ, Angle from Surface Normal
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
0
10
20
30
40
50
60
70
80
90
XBL 7312-7142

Fig. 2a.

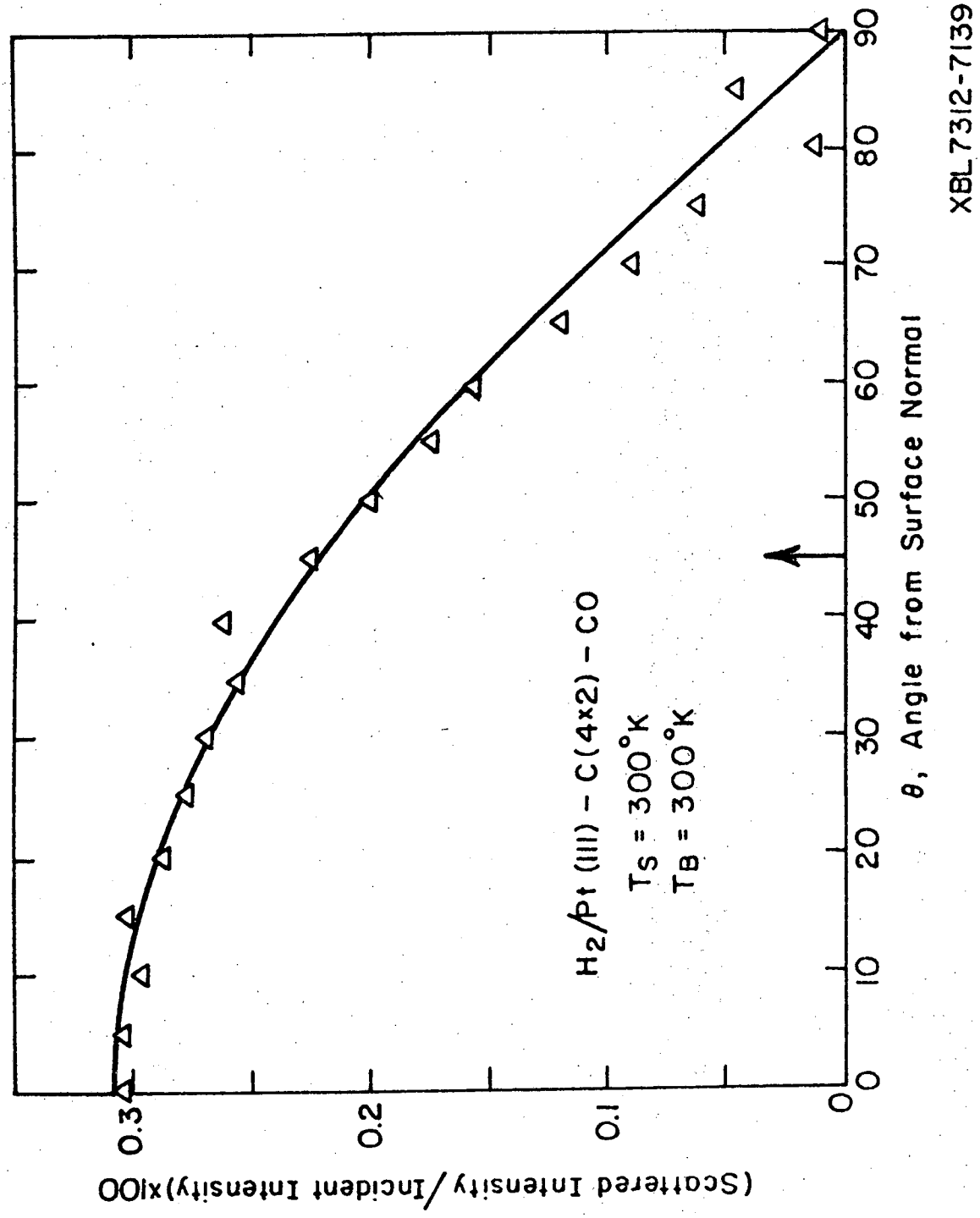
(Scattered Intensity/Incident Intensity)x100
0.3
0.2
0.1
0
0
10
20
30
40
50
60
70
80
90
θ, Angle from Surface Normal
H2/Pt (111) - C(4x2) - CO
TS = 300°K
TB = 300°K
XBL 7312-7139

Fig. 2b.

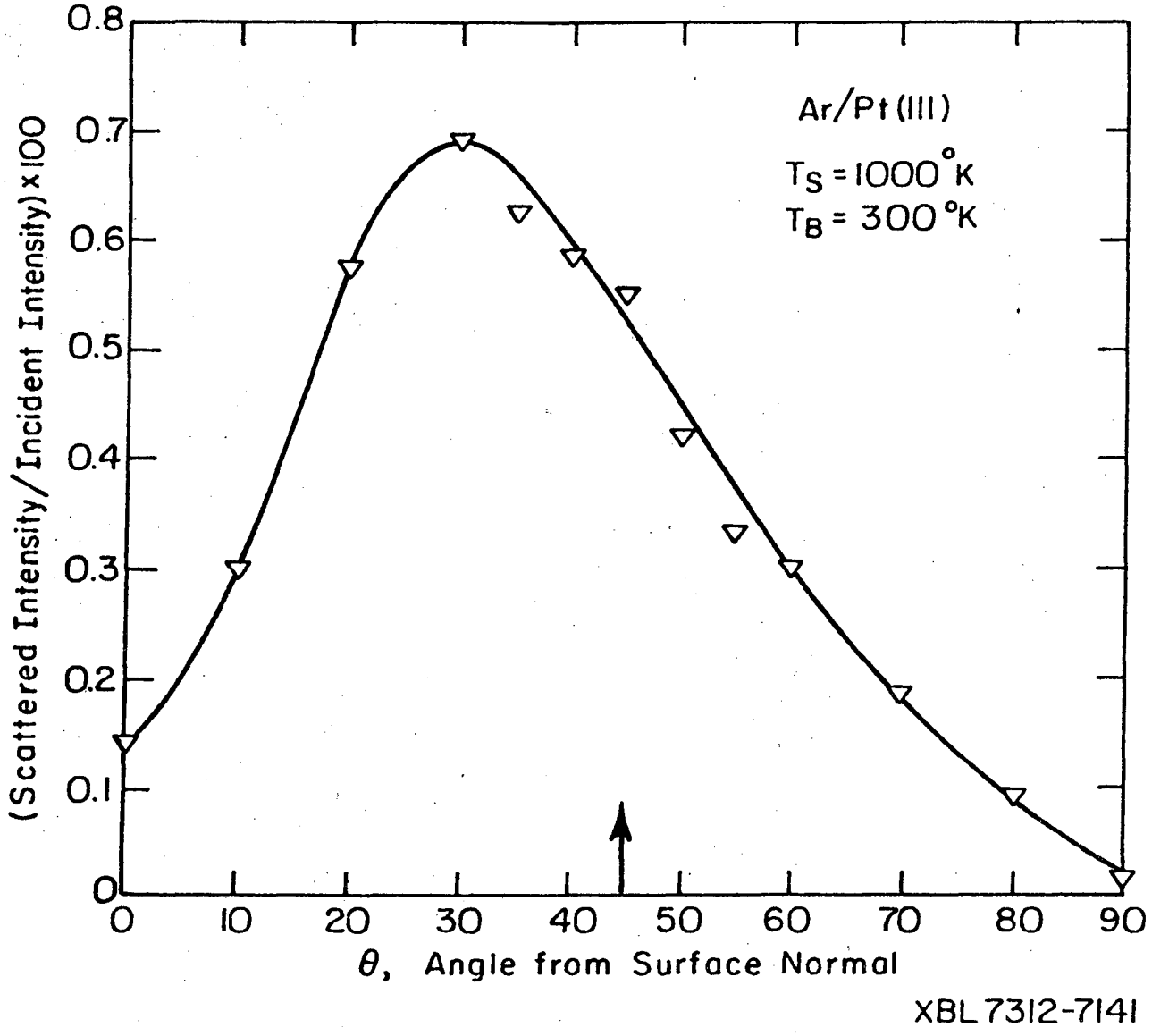
Ar/Pt(111)
T_S = 1000°K
T_B = 300°K
(Scattered Intensity/Incident Intensity) x 100
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
10
20
30
40
50
60
70
80
90
θ, Angle from Surface Normal
XBL 7312-7141

Fig. 3a.

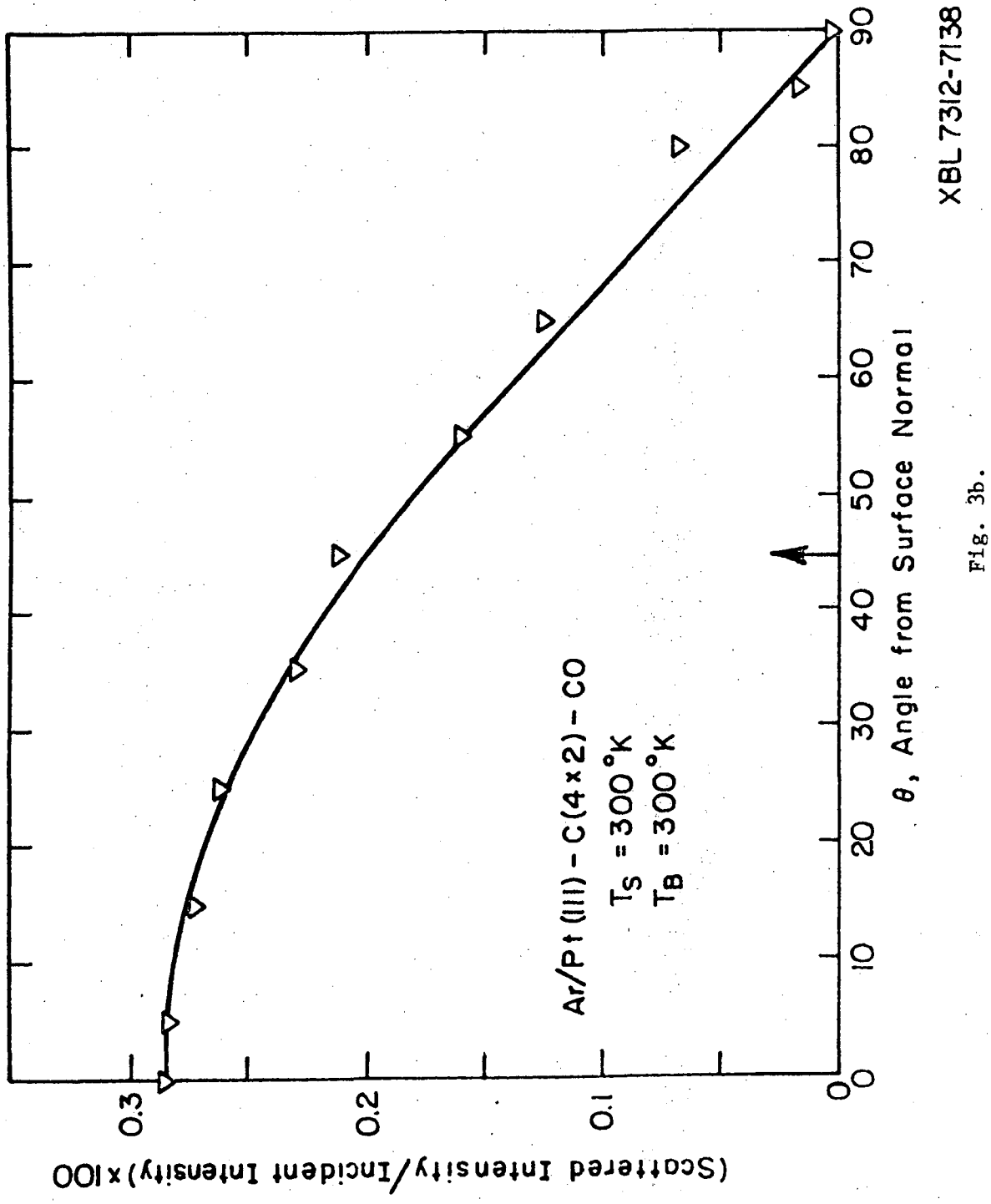
(Scattered Intensity/Incident Intensity) x 100
0.3
0.2
0.1
0
0
10
20
30
40
50
60
70
80
90
θ, Angle from Surface Normal
Ar/Pt (111) - C(4 x 2) - CO
T_S = 300 °K
T_B = 300 °K
XBL 7312-7138

Fig. 3b.

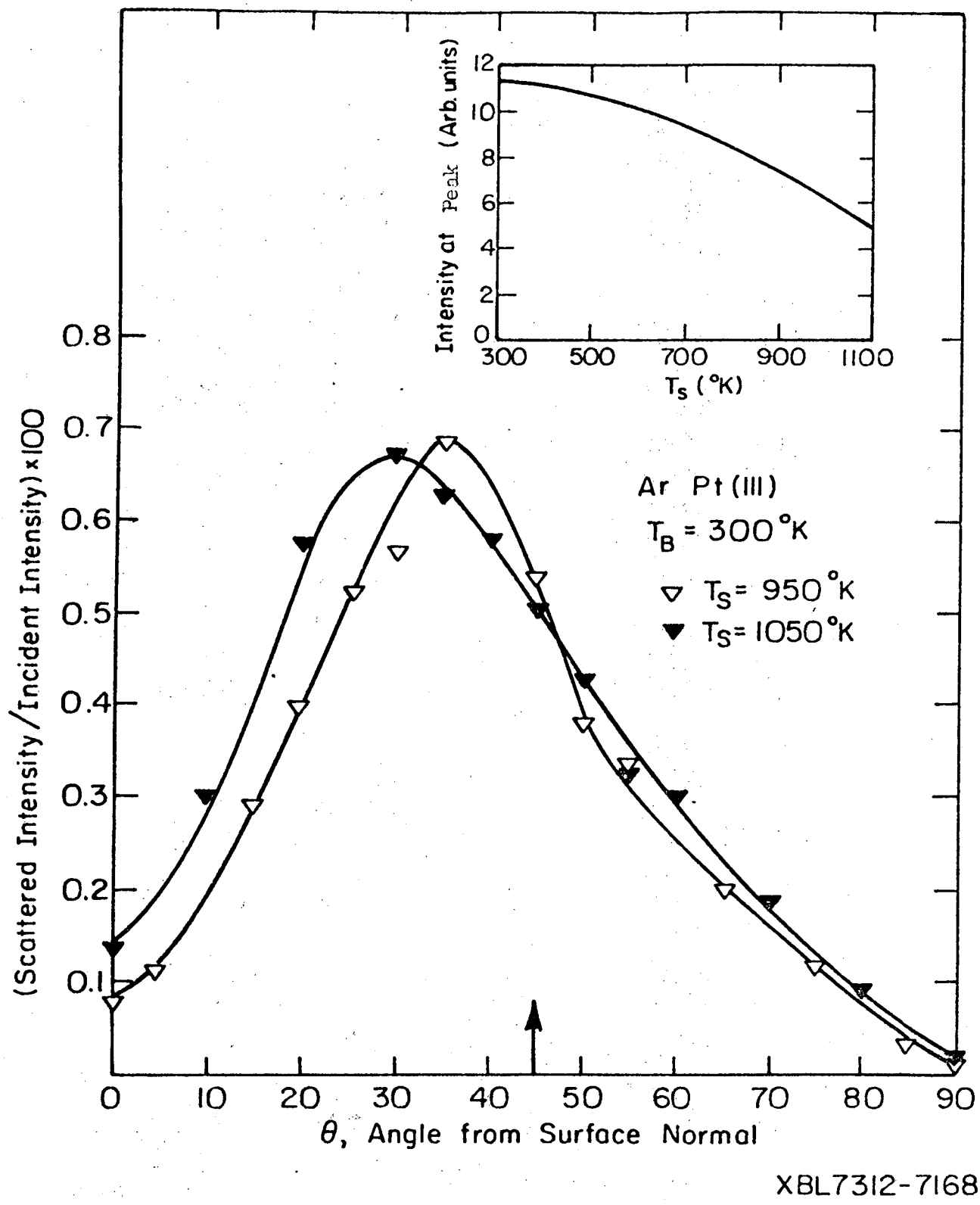
Intensity at Peak (Arb. units)
12
10
8
6
4
2
0
300
500
700
900
1100
T_S (°K)
(Scattered Intensity/Incident Intensity) x100
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
Ar Pt(111)
T_B = 300°K
T_S = 950°K
T_S = 1050°K
0
10
20
30
40
50
60
70
80
90
θ, Angle from Surface Normal
XBL7312-7168

Fig. 4.

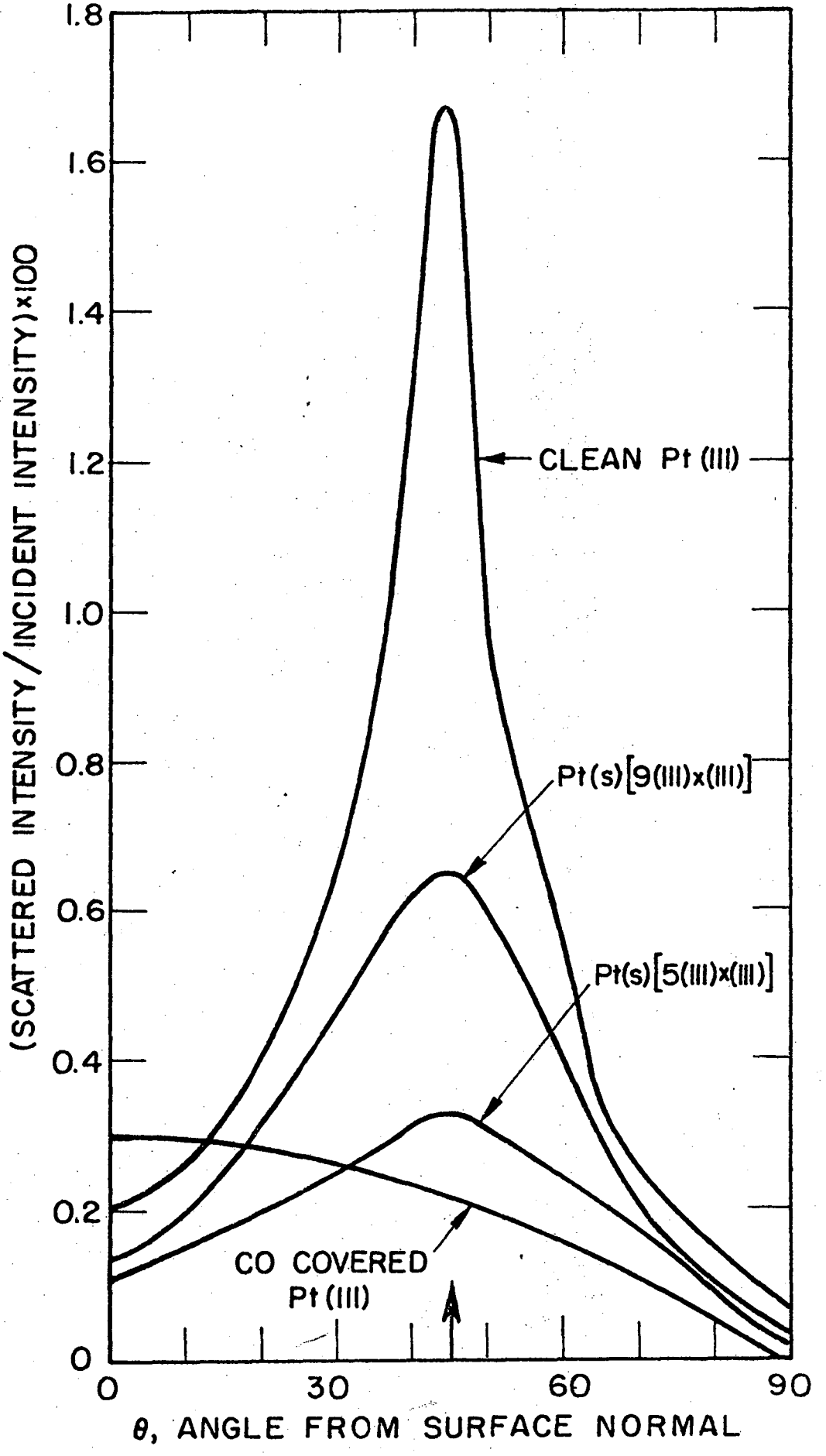

Fig. 5. XBL 743-5678

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