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Nicolás García, Larry L. Kesmodel, J. Solana, and N. Cabrera

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NEW INTERPRETATION OF ELECTRON DIFFRACTION DATA FOR Al IN TERMS OF LENNARD-JONES TYPE SURFACE STATE RESONANCES

by

Nicolás García[+]

Department of Physics* University of California, Berkeley, California 94720

and

Larry L. Kesmodel

Department of Chemistry, University of California and
Inorganic Materials Research Division,[§] Lawrence Berkeley Laboratory,
Berkeley, California 94720

and

J. Solana and N. Cabrera

Departamento de Física, Universidad Autónoma de Madrid
Canto Blanco (Madrid) Spain

Abstract

An analysis of low-energy electron diffraction rotation diagrams for the Al(001) surface at E = 20 eV is made using an accurate multiple-scattering model. We show for the first time that detailed agreement is achieved for all features of the experimental data relating to simple multiple-scattering processes. However, we propose that the sharp resonance structure in the specular beam data is associated with localized surface electronic states via a Lennard-Jones type resonance scattering.

In 1971 Lauzier et al.[1] reported interesting results of low-energy electron diffraction (LEED) rotation diagram experiments for the clean (001) surface of Al. In a rotation diagram experiment, the beam intensity (denoted by $I(\phi)$) is measured as a function of the azimuthal angle ϕ, while the polar angle θ and the energy E are held constant. The interest in this method lies in the fact that all structure in the $I(\phi)$ curves is, in principle, due to multiple-scattering effects or resonance effects and the (00) beam is generally smooth. This is in contrast to the more common intensity vs. energy (I-V) profiles (E varied, θ and ϕ fixed), which show pronounced kinematic (single-scattering) interference peaks as well as strong multiple-scattering features and which are widely used for surface structure analysis. The experiment of Lauzier et al. generated considerable interest because of the presence of sharp, resonancelike structure in the (00) beam $I(\phi)$ curve for E = 20.8 eV which persisted over a wide range of θ and ϕ. This structure was seen to be of the Breit-Wigner form and was partly associated with emergence conditions (threshold effects) of certain non-specular beams. On this basis, Lauzier et al.[1] suggested

that the observed structure was possibly due to some kind of surface resonance, but did not give a clear explanation of the data and deferred further comment until multiple-scattering calculations were performed. Unfortunately, these subsequent calculations gave either very poor[2] or only marginal[3,4] agreement with the I(ϕ) curves at E = 20.8 eV, θ = 50° where the resonance structure was clearly observed. This caused further confusion over the nature of this structure, i.e., whether it is associated with simple multiple scattering events, threshold effects, or surface resonances.

In this Letter we clarify the results of Lauzier et al. and give a physical interpretation of their data; (i) we present for the first time calculations of the I(ϕ) curves which show detailed agreement with experiment for those features relating to simple multiple-scattering events, (ii) we assert, in contrast, that the resonancelike features are associated with localized states and support this with a model calculation, and (iii) we show that further important aspects of the data are in agreement with electronic surface states calculations for the Al(001) surface.[5]

We first consider the calculation of the I(ϕ) curves. We employ a T-matrix multiple-scattering method of LEED which has yielded accurate descriptions of I-V profiles of several materials, most recently of Pt.[6] The real part of the scattering potential was characterized by five phase shifts from the Snow self-consistent Hartree-Fock-Slater potential.[7] The effect of inelastic collisions was treated with a parameterized form of the imaginary part of the self-energy Σ_2 = 2 eV from electron gas calculations[8] for E $\gtrsim$ 20 eV above the vacuum level. Bulk values were

used for the lattice distances and the Debye temperature describing vibrational effects. The only adjustable parameter used was the inner potential, V_o, and the value V_o = 11 eV was found to give by far the best fit to the $I(\phi)$ curves in agreement with the optimum value found independently[9] in matching I-V profiles in the low-energy region. An important point for this discussion is that our method of calculation includes lattice multiple-scattering and threshold effects, but neglects the effects of surface states which must be treated by matching of wave-functions at the vacuum-solid interface.

Figure 1 shows the results of our calculations as compared to the experiment. In the data for the (00) beam for $\theta = 50°$ there is a sharp resonance (R_1) at $\phi \simeq 30°$ and a much weaker one (R_2) at $\phi \simeq 38°$.[10] The calculation reproduces all features in the experimental curves with surprising accuracy <u>except</u> these resonance structures. This is in contrast to previous work[2-4] which failed to describe accurately not only the resonance structure, but also the additional features. There is also a weak structure (T) near $\phi \simeq 25°$ which we found to be insensitive to V_o in position and which is clearly a threshold effect directly related to the vacuum submergence of the $(\bar{1}\bar{1})$ beam.[11] This threshold structure was present in previous work[3,4] at $\phi \simeq 25°$, and it is not to be confused with the R_1 resonance. We also made calculations (Figure 3 below) for $\theta = 40°$ with excellent agreement with experiment.

The conclusion to be reached from the above results seems clear. Our calculation has described in great detail all multiple-scattering features in the data except those which it explicitly neglects, namely those associated with surface states. We, therefore, propose a

connection between these states and the resonance structure in the $I_{00}(\phi)$ curve, and we give below further evidence for this interpretation. The model we consider has a rather direct analogy with the resonances discussed by Lennard-Jones[12] in connection with atom-surface scattering, first observed by Frisch and Stern,[13] and present in recent atom-surface scattering theories.[14] In this model, the incident particle or wave is diffracted by a $\underset{\sim}{g}$-beam (surface reciprocal lattice vector)parallel to the surface and becomes "trapped" in the potential well perpendicular to the surface. More explicitly, we may write,

$$\underset{\sim}{k}_{\parallel}' = \underset{\sim}{k}_{\parallel} + \underset{\sim}{g} \tag{1}$$

and

$$k_{\underset{\sim}{g}z}^{2} = 2mE/\hbar^{2} - (\underset{\sim}{k}_{\parallel} + \underset{\sim}{g})^{2} \tag{2}$$

where $\underset{\sim}{k}_{\parallel}$ and $\underset{\sim}{k}_{\parallel}'$ refer to incident and diffracted wavevector components parallel to the surface and $k_{\underset{\sim}{g}z}$ refers to the diffracted component perpendicular to the surface for the $\underset{\sim}{g}$ beam. Suppose that a surface state satisfies the dispersion relation

$$E_s(\underset{\sim}{k}_{\parallel}) = \varepsilon + \hbar^{2}(\underset{\sim}{k}_{\parallel} + \underset{\sim}{g})^{2}/2m \tag{3}$$

Here ε refers to the surface state energy calculated from an appropriate surface potential averaged over the planar directions (the surface state energy at the Γ point in the two-dimensional surface Brillouin zone (SBZ)) and the second term describes free electron dispersion in the plane. It has been shown[15] that resonance scattering can occur when $k_{\underset{\sim}{g}z}^{2}$ in Eq.(2) approaches $2m\varepsilon/\hbar^{2}$ in Eq.(3). Of course, the real state will not exhibit free-electron behavior and Eq.(3) becomes a secular equation when all $\underset{\sim}{g}$-vectors

are included. Therefore, ε (roughly speaking, a kind of energy component normal to the surface) is not constant and depends on $\underset{\sim}{k}_{\parallel}$.

We show in Figure 2 how these considerations relate to the diffraction data of Ref. 1. In Figure 2a we have plotted $\underset{\sim}{k}_{\parallel}$ from the (θ,ϕ) coordinates[1] of the observed resonances, and we have mapped them to the irreducible element of the SBZ. In Figure 2b we plot the corresponding values of ε determined from Eq.(2)-(3) in eV below the vacuum level with $\underset{\sim}{g} = (\bar{1}\bar{1})$. The path in the SBZ of Figure 2a essentially turns back on itself near the point labelled 5, and we see that the values of ε also show this symmetric behavior. Furthermore, the values of ε are in agreement with surface electronic states calculations for Al[5] which show a surface state gap 9-10 eV above the band minimum at Γ. Using $\varepsilon = -2.5$ eV from Figure 2, we arrive at a corresponding value of 10-11 eV for the surface states, taking into account the inner potential correction.

From the above considerations the wavevector component of the scattered electron perpendicular to the surface should acquire a decay constant γ describing surface state attenuation into the solid in contrast to propagating bulk states. This suggested to us an approximate method of including the resonance effect in the multiple-scattering program. In this model the terms describing the propagation between layers of the intermediate scattered beam $\underset{\sim}{g}$ are modified near the resonance condition by giving an attenuation factor γ to these waves in addition to the inelastic-collision attenuation. In Figure 3 we show the results using $\gamma = .06$ Å^{-1} which is representative of γ values for Al surface states calculations.[5] We see that this seemingly small change in the interlayer scattering propagator (which contains the collective effects of many beams)

produces changes in the intensities at the resonance angles in good agreement with experiment. Furthermore, for $\theta = 50°$ the R_1 resonance caused by the $(\bar{1}\bar{1})$ beam is much stronger than the R_2 resonance associated with the (02) beam, also in agreement with experiment. This is due to the much greater intensity of the $(\bar{1}\bar{1})$ beam as compared to the (02) beam. The effects on the other beams are insignificant as shown in experiment. Calculations made for $\gamma = .20\ \text{Å}^{-1}$ gave proportionately larger intensity changes. We emphasize that we have incorporated one aspect of the physics in this model, but we do not purport to describe the detailed shape of the resonance.

In conclusion, considering the strong evidence that we give in our surface state interpretation we suggest the possibility of using LEED rotation diagrams to locate the positions of both occupied and unoccupied electronic surface states. Also, this is the first analysis of experimental data that evidences the existence of surface states in metals and the method seems promising also for determination of surface states near the bottom of the valence band, since few experiments now exist for such states. Experiments are in progress to study this question.

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11. In Figure 2 of Ref. 1, the $(\bar{1}\bar{1})$ beam was plotted with the angle $\phi' = 45 - \phi$ and the $(\bar{1}\bar{1})$ beam is therefore shown emerging at $\phi' \simeq 20°$.

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Figure Captions

Fig. 1. Comparison of experimental[1] and calculated (dashed line) rotation diagrams for E = 20.8 eV, $\theta = 50°$ for Al(001). The experimental curves are normalized to theory at $\phi = 45°$ for the (00) and $(\bar{1}1)$ beams and at $\phi = 20°$ for the $(\bar{1}\bar{1})$ beam. The labels T, R_1, R_2 refer to threshold and resonance effects (see text). V_o is the inner potential above the APW muffin-tin zero.

Fig. 2. (a) Plot of the experimental (Ref. 1, Figure 3) positions for $\underset{\sim}{k}_{\parallel}$ and mapping to SBZ. The arc shown describes a circle of constant $|\underset{\sim}{k}_{\parallel}(5) + \underset{\sim}{g}(\bar{1}\bar{1})|$. The points departing from this arc indicate dispersion in ε(see Eq.(3)).

(b) Values of ε determined from the experimental data and Eqs.(2)-(3) corresponding to the points in (a).

Fig. 3. Comparison of theory (dashed line) and experiment[1] for E = 20.8 eV. The model gives the resonance structure R_1, R_2 by inclusion of additional surface state damping γ(see text).

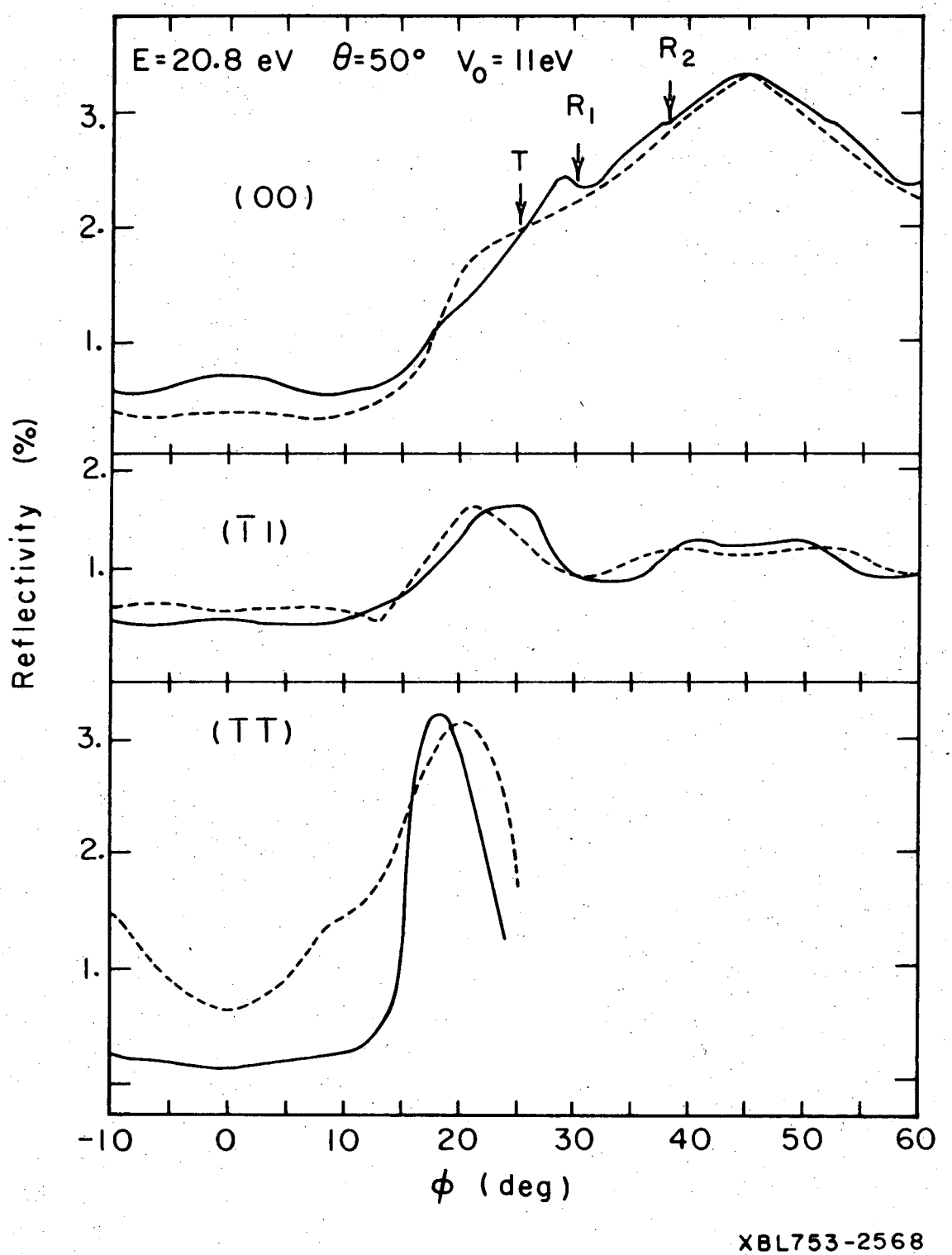
E=20.8 eV θ=50° V0= 11eV
R2
R1
T
(00)
(T̄1)
(TT)
Reflectivity (%)
3.
2.
1.
-10
0
10
20
30
40
50
60
φ (deg)
XBL753-2568

Figure 1

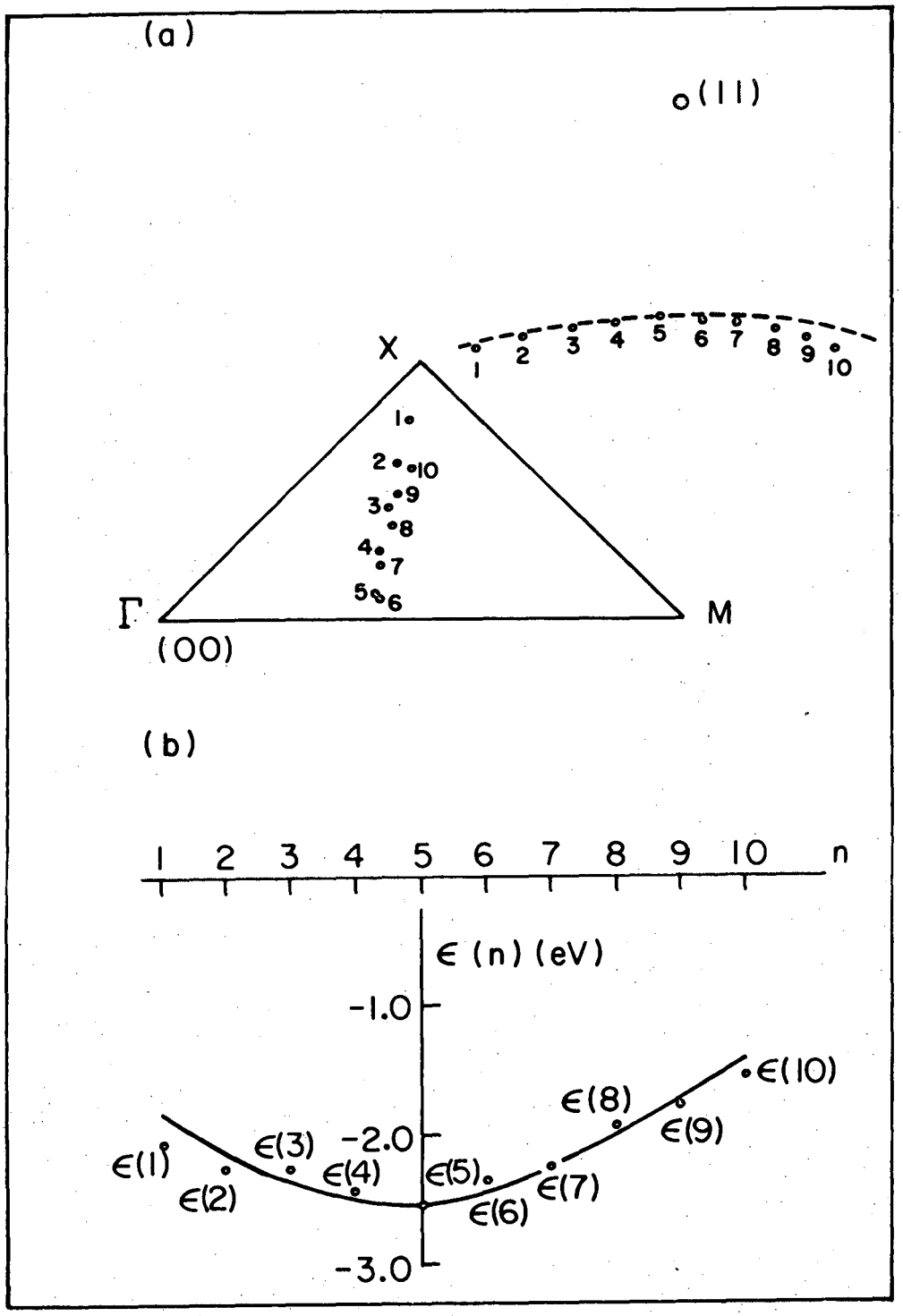

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Figure 2

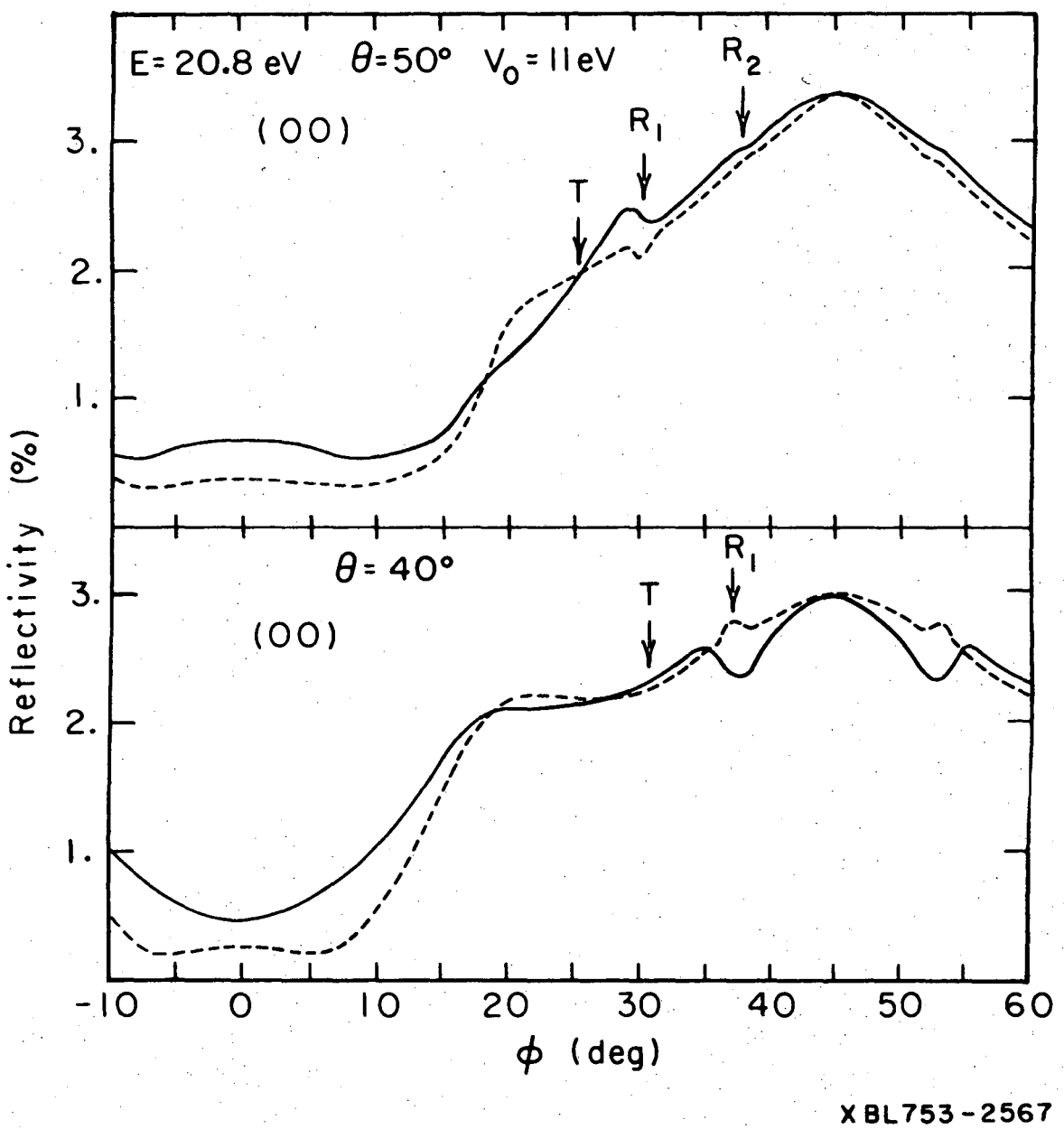
E= 20.8 eV θ=50° V0 = 11eV
(00)
T
R1
R2
θ= 40°
(00)
T
R1
Reflectivity (%)
3.
2.
1.
-10
0
10
20
30
40
50
60
φ (deg)
XBL753-2567

Figure 3

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