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THE USE OF ATOMIC SCATTERING FACTORS IN CALCULATIONS OF LOW ENERGY ELECTRON DIFFRACTION BEAM INTENSITIES

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ABSTRACT

The use of computed atomic scattering factors for free atomic potentials is proposed for purposes of surface structure analysis in low energy electron diffraction calculations. Atomic scattering factors for low energy elastic electrons are presently available in the relativistic Hartree-Fock-Slater approximation. Calculations for bismuth and lead are shown to agree favorably with vapor phase measurements of the differential cross section at electron energies in excess of 50 eV. Evidence is cited from low energy electron diffraction experiments with liquid mercury and tin surfaces, indicating that the back reflected electron intensities are very similar to calculated intensities for scattering from the free atoms. The effect of the liquid structure factor is investigated and shown to account for less than 15% of the reflected electron intensity from a liquid bismuth surface. The atomic scattering factors for electrons from atoms in the vapor and condensed

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phases differ most notably in the shapes and magnitudes of the respective forward scattering peaks. These differences are associated with the inclusion of many phase shifts (~50) representing the large angular momentum values necessary to adequately describe the peripheral atomic collisions in the vapor phase. It is argued that for structure analysis calculations it should be sufficient to use atomic scattering factors computed for isolated atomic potentials with the inclusion of a smaller number (~5) of phase shifts, in order to approximate the solid phase electron scattering factors.

INTRODUCTION

Analysis of the intensities of low energy electron diffraction (LEED) beams that are back-diffracted from solid surfaces appears to be capable of providing detailed structural information about periodic surfaces. Much experimental and theoretical effort has been put forth in the attempt to compare measured diffracted beam intensities to realistic scattering models in order to extract information on the three dimensional structure of surfaces and adsorbed surface layers. Multiple scattering theories which include the effects of inelastic damping have recently been successful in reproducing the major features of experimental intensity vs incident electron energy curves for a number of elastic diffraction beams in aluminum,[1,2,3] silver[2] and copper.[2,3]

In these theories the electron-solid interaction is accounted for and enters the formalisms by means of pseudopotential parameters[4,5] or energy dependent phase shifts.[6,7] Scattering of the incident electron beam occurs primarily in the vicinity of the atomic centers of the crystal, whose potential distribution is somewhat modified from the free atomic potential due to redistribution of electronic charge in the valence and conduction bands. In this paper we consider the direct use of isolated atomic scattering factors as an approximation to the true scattering potential for LEED structure calculations. We utilize the calculated atomic scattering factors of Fink and Yates[8,9] that will be shown to compare well with experimental gas phase scattering data where such data are available. We then review the experimental work on back scattering of low energy (40-200 eV) electrons from liquid metal

surfaces, and compare the results to those predicted from the use of calculated atomic scattering factors.

It appears that the use of atomic potentials is justified for use in the theoretical scattering models presently being employed to analyze the intensities of elastic back scattered low energy electron beams. Due to the large momentum transfer of back diffracted electrons scattered from crystal or liquid metal surfaces, variations in the atomic potential that occur in the vicinity of the nuclear charge and core electrons are most important in determining the angular distribution of the back scattered beam.[10] Thus, alterations in the atomic potential due to the spatial redistribution of outer shell electrons when atoms are combined to form a condensed phase are not expected to play a large role in determining the angular distribution of the back scattered low energy electrons.

CALCULATED ATOMIC SCATTERING FACTORS

Atomic scattering factors, $f(\theta,E)$, have been calculated for a large number of elements by Fink and Yates.[8] They employ atomic potentials derived from the relativistic Hartree-Fock-Slater wavefunctions of Liberman and coworkers.[11] The Dirac equation for an incident electron in a static atomic potential is solved numerically to yield scattering phase shifts as a function of incident electron energy. In these calculations exchange and polarization effects between the incident and atomic electrons are not included. Both of these effects become increasingly important at incident electron energies below 100 eV, and failure to include them has been shown to lead to serious disagreement with experiment in the energy range below 30 eV.[12] It is for this reason that we restrict our consideration of low energy electrons to those in excess of 40 eV. This in no way impairs the use of these atomic scattering factors for surface structure calculations using low energy electron diffraction since a large amount of structural information can be obtained in the energy range 50 to 200 eV. For additional discussion of the approximations employed in this phase shift calculation, and on the breakdown of the static potential approximation at low incident electron energies, the reader is referred to the original sources.[8,9,12]

The extent of the agreement between experimentally measured differential cross sections in the vapor phase and the calculated atomic scattering intensities $|f(\theta,E)|^2$ for Au and Bi is illustrated in Fig. 1. Since these curves do not represent absolute intensities, the experimental and theoretical curves have been normalized at a maximum point

of $|f(\theta,E)|^2$ for each energy. Agreement is good for energies in excess of 100 eV, while the neglect of exchange and polarization effects becomes increasingly evident at lower energies. At 50 eV the shape of the Bi cross section curve reproduces well the scattering into the back hemisphere, but the forward scattering portion of the curve is in poor agreement with the experimental work. The effects of this known inaccuracy in the forward scattering peak at low energies is not as serious a problem as it may at first appear for application to LEED calculations, as long as the atomic scattering factor is reasonably accurate at large angles. This point will be discussed in detail in a later section.

ELECTRON BACK SCATTERING FROM DISORDERED SURFACES

Information concerning the atomic scattering factors suitable for use in LEED calculations can be gained from observation of back scattered electron intensities from disordered surfaces. Atomic scattering properties are more directly observable experimentally when the phase coherence of the diffracted beam, as expressed in the structure factor, is averaged in the absence of long range order. Multiple scattering and inelastic damping processes are not diminished for electrons scattered from disordered surfaces and must be corrected for, in order to separate out the single scattering portion of the observed intensities. Schilling and Webb[10] have made such a correction and applied it to low energy electron diffraction from liquid mercury. Their experimental intensities, when corrected for multiple scattering and inelastic effects, show remarkable agreement with the results obtained by scattering low energy (100-500 eV) electrons from mercury vapor over the angular range $\theta = 60°$ to $170°$ from the incident beam direction.

Additional evidence for the validity of using calculated atomic scattering factors in LEED calculations is obtained from experiments of Goodman and Somorjai[13] who observed back diffracted low energy electron intensities from a liquid tin surface. Their results are reproduced in Fig. 2a showing the elastic electron intensity contours as a function of energy and scattering angle. For comparison, the atomic scattering intensity $|f(\theta,E)|^2$ is calculated and plotted in a similar manner in Fig. 2b. It will be noted that while the general features are in agreement, the ratios of the maxima to the minima are less

pronounced in the experimental liquid scattering results than in the calculated atomic intensity plot. Application of the two approximations of Schilling and Webb[10] to correct for multiple scattering and inelastic damping have the effect of smoothing the intensity profiles obtained from the atomic calculation and bringing it into close agreement with the intensity contours of the liquid scattering experiment.

Experiments similar to that with liquid tin have been carried out with liquid lead and bismuth,[13] but the results do not seem to be simply related to the calculated atomic scattering factors. A discussion of probable causes for this disagreement is included in the appendix.

DISCUSSION

Due to the geometry of the LEED apparatus, which detects only back scattered electrons, the momentum transfer $\hbar \underset{\sim}{q}$ is such that $|\underset{\sim}{q}| \gtrsim 5$ Å^{-1} for incident electron energies in excess of 40 eV. Variations in the crystal potential occurring in the immediate vicinity of a nuclear charge and its core electrons furnish the largest contribution to the back scattered intensity in this range of momentum transfer.[10] Thus, changes in the details of the potential due to the spatial redistribution of outer atomic electrons, when combined to form a condensed phase, and structural effects related to the liquid radial distribution function, are not expected to play a large role in determining the angular distribution of the back scattered electrons. The agreement between the scattering intensities of electrons from liquid mercury and tin surfaces and the calculated and experimentally observed atomic scattering intensities, discussed in the previous section, illustrates this observation.

The contribution of the radial distribution function to the total reflected electron intensity from a liquid bismuth surface is illustrated in Fig. 3. The liquid structure factor $I(\underset{\sim}{q})$, which is the Fourier transform of the radial distribution function, contributes a coherent component to the scattered intensity that is superposed on the incoherent (atomic) part of the total intensity. The experimentally determined liquid structure factor for bismuth[14] is plotted for back scattered electrons as a function of the elastic electron energy in the lower portion of Fig. 3. The upper portion of the same figure reproduces a contour plot for elastic electron intensities reflected from a liquid bismuth surface.[13] The dashed lines in the upper plot correspond to

two maxima of the liquid structure factor. The expected ridge structures along these maxima are visible at electron energies less than 25 eV, and are weaker at higher energies. In Fig. 4 we have plotted three sections from the contour map of liquid bismuth, corresponding to electrons that are reflected through angles of 150°, 160° and 170°. In the same figure we include for comparison the liquid structure factor I(q). It appears that the liquid structure factor accounts for less than 15 per cent of the total reflected electron intensity. This liquid bismuth data[15] represents the first direct experimental observation of the effect of the liquid structure factor on LEED intensities. Results reported for elastic electron scattering from liquid tin and lead[13] show no such clear indication of liquid structure.

On the other hand, electron scattering in the forward direction occurs with small momentum transfer and is very sensitive to variations in the potential over a layer region which includes the outer shell electrons as well. Atomic scattering calculations show sharp forward peaks due mainly to the region of small electron charge density far from the nucleus. The forward scattering peak in the condensed phase will be considerably altered from the atomic scattering intensities for two reasons; 1) The superposition of several atomic potentials, mostly near the Wigner-Seitz cell boundary in the solid or liquid drastically changes the overall potential from the free-atom exponential-tail form. 2) The spatial redistribution of valence and conduction electrons over the Wigner-Seitz cell alters the atomic potential most noticeably in the regions midway between two nuclei. The forward scattering peaks in condensed matter are thus expected to differ from

those predicted by atomic calculations or found experimentally in the scattering of electrons from atoms in the gas phase.

The computer program of Fink and Yates[8] truncates the phase shift calculation at an ℓ-value for which the phase shifts δ_ℓ and $\delta_{-\ell-1}$ are less than 10^{-6} radians, which corresponds to maximum angular momentum values of $\ell \lesssim 50$. This large number of phase shifts is required in order to build up the realistically sharp forward elastic peak found in atomic scattering of electrons. It is found, however, that a much smaller number of phase shifts ($\ell \lesssim 10$) is required below energies of 200 eV to construct atomic scattering factors that are good approximations to the more exact ones, except that the forward scattering peaks are less intense and less sharply peaked.

The inclusion of a large number of phase shifts in the scattering factor calculations for atoms in the condensed phase is physically unrealistic since this accentuates the forward scattering peak which is a consequence of the peripheral collisions of atomic scattering. In the condensed phase, the atom-like potential[15] can be considered to be truncated near the Wigner-Seitz cell radius r_o, and the phase shift δ_ℓ will be negligible for an incident electron wavevector $\underset{\sim}{k}$ if $\ell \gg kr_o$[16]. The scattering factor $f(\theta,E)$ at a given incident electron energy E, is approximated by a number of terms in the partial wave expansion. In order to achieve similar accuracy at higher energies, the number of terms retained must be increased proportionally to $|\underset{\sim}{k}|$.

The forward scattering peak shape and magnitude arrived at in this way is only a first approximation to the actual angular distribution

of forward scattered electrons in a solid, although it well represents the distribution of the back scattering events. At the present stage of development, LEED calculations are unable to utilize more than four to eight phase shifts in a practical calculation due to excessive computer time requirements. Since the immediate goal of such calculations is to determine the surface structure and not to probe the details of the interatomic potential, we believe that the use of accurate atomic scattering factors is justified.

APPENDIX

Disagreement between the experimental and calculated back scattering intensities for liquid lead and bismuth has been noted in the previous section, although good agreement exists in the cases of liquid mercury and tin. Direct comparison of the theoretical scattering intensities for atomic bismuth and the experimental vapor phase scattering data presented in Fig. 1 indicates that the calculated intensities are quite accurate, although no such experimental data are available for lead.

A striking feature of the liquid bismuth data is illustrated in Fig. 5 where we plot sections corresponding to reflected electron intensities at constant electron energies from the contour map of Fig. 3. A prominent ridge structure showing a maximum intensity for electrons reflected between 155° and 160° from the incident beam direction persists throughout the energy range. It is doubtful that such an energy independent structure at a constant emission angle can be due to electron-scattering dynamics. It is more likely that this ridge is of geometrical origin, perhaps being due to specular reflection of the electron beam from irregularities (i.e., surface waves) at the liquid surface.

FOOTNOTES AND REFERENCES

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15. The atom-like potential differs from a true atomic potential due to the additive contribution from the exponential tails of

neighboring atomic potentials. The differences are most pronounced in the region midway between atomic centers near the Wigner-Seitz cell boundary. In using calculated atomic scattering factors we approximate the atom-like potential by the atomic potential.

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FIGURE CAPTIONS

Fig. 1 Experimental differential cross section measurements (dashed curves)[17,18] are compared to calculated atomic scattering intensities $|f(\theta,E)|^2$ (solid curves)[8] for Au and Bi at four incident electron energies. The experimental values are relative measurements are are normalized to the calculated curves at each energy.

Fig. 2a Electron back scattering intensities from a liquid tin[13] surface represented as a contour plot. Incident electron energy is plotted along the abscissa and the scattering angle measured from the direction of the incident beam is plotted along the ordinate. The relative intensity contours are labeled in arbitrary units.

Fig. 2b Calculated atomic scattering intensity for low energy elastic electrons from tin atoms represented as a contour plot for comparison with Fig. 2a.

Fig. 3 The bottom portion of the figure represents the liquid structure factor $I(\underset{\sim}{q})$[14] for 180° back scattered elastic electrons from liquid bismuth as a function of electron energy. The upper portion of the figure is taken from Goodman and Somorjai[13] and is a contour plot for back reflected electron intensities from a liquid bismuth surface similar to Fig. 2a. The sloping dashed lines in the upper plot represent lines of constant momentum transfer $|\underset{\sim}{q}|$ whose values correspond to maxima in the $I(\underset{\sim}{q})$ curve.

Fig. 4 Reflected electron intensity from a liquid bismuth surface as a

function of incident electron energy. The three solid curves are intensities measured at angles of 150°, 160° and 170° from the direction of the incident beam. The dashed curve shows the liquid structure factor $I(\underset{\sim}{q})$ for comparison, and is not plotted to the same scale as the solid curves.

Fig. 5 Reflected electron intensity from a liquid bismuth surface as a function of scattering angle for incident electrons at five energies. The ridge structure in the reflected intensity appear between 155° and 160° throughout this energy range.

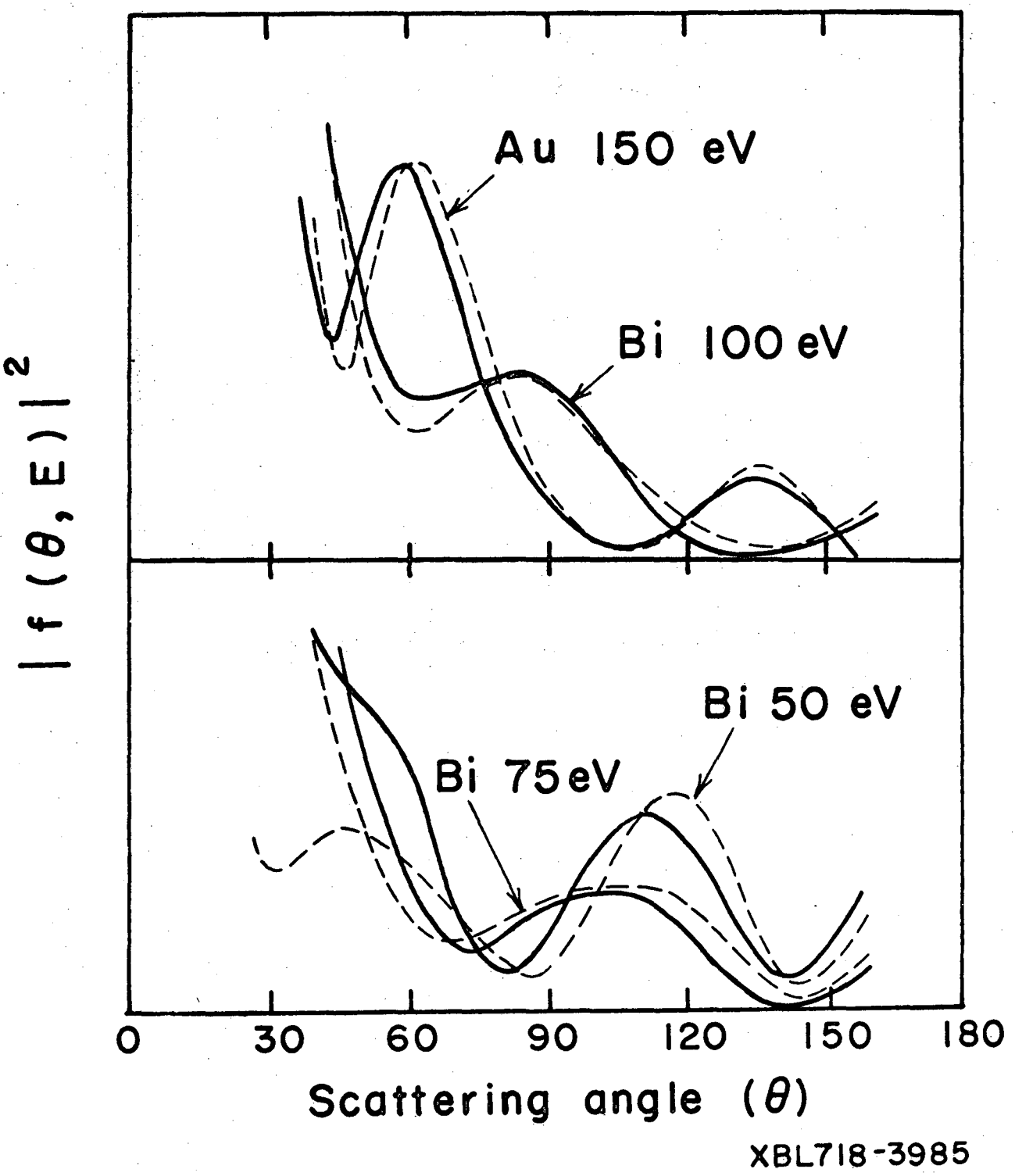
Au 150 eV
Bi 100 eV
Bi 50 eV
Bi 75 eV
$|f(\theta, E)|^2$
0
30
60
90
120
150
180
Scattering angle (θ)
XBL718-3985

Fig. 1

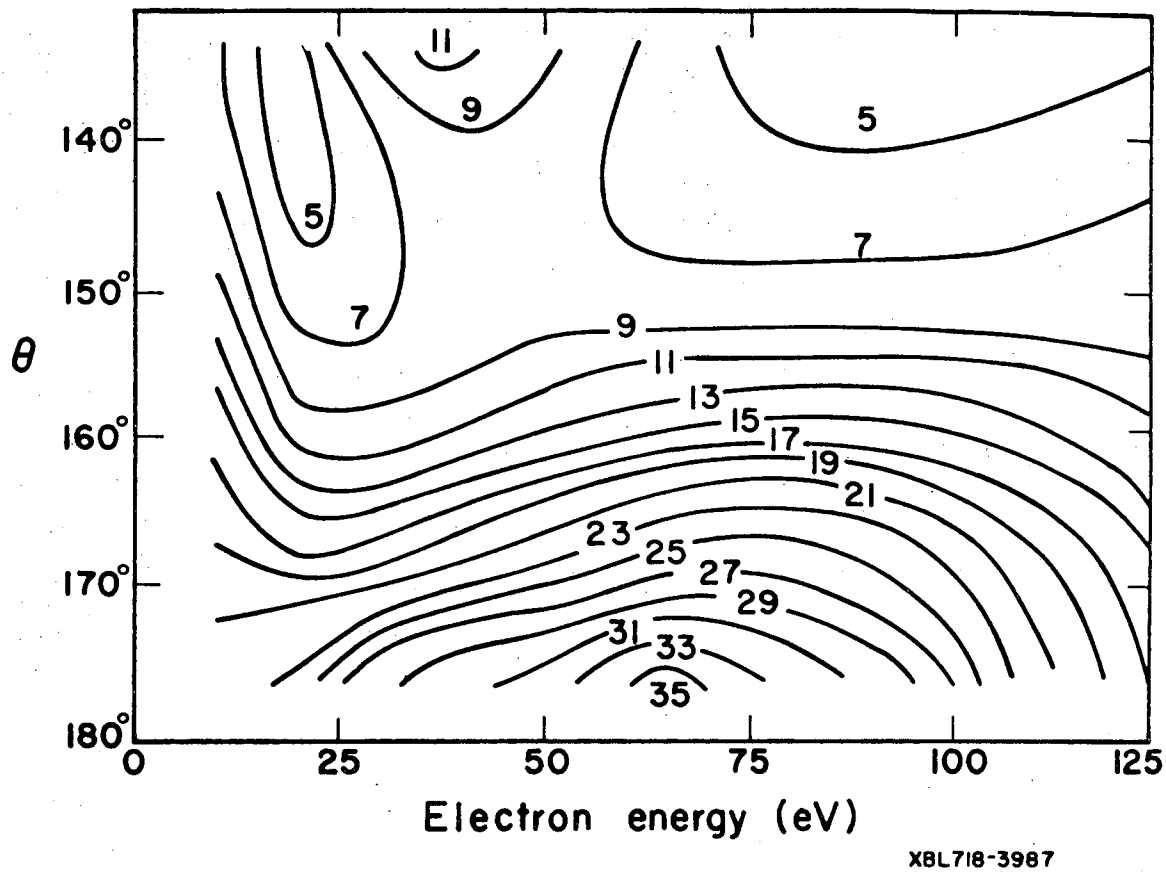
11
9
5
5
7
7
9
11
13
15
17
19
21
23
25
27
29
31
33
35
140°
150°
160°
170°
180°
θ
0
25
50
75
100
125
Electron energy (eV)
XBL718-3987

Fig. 2a

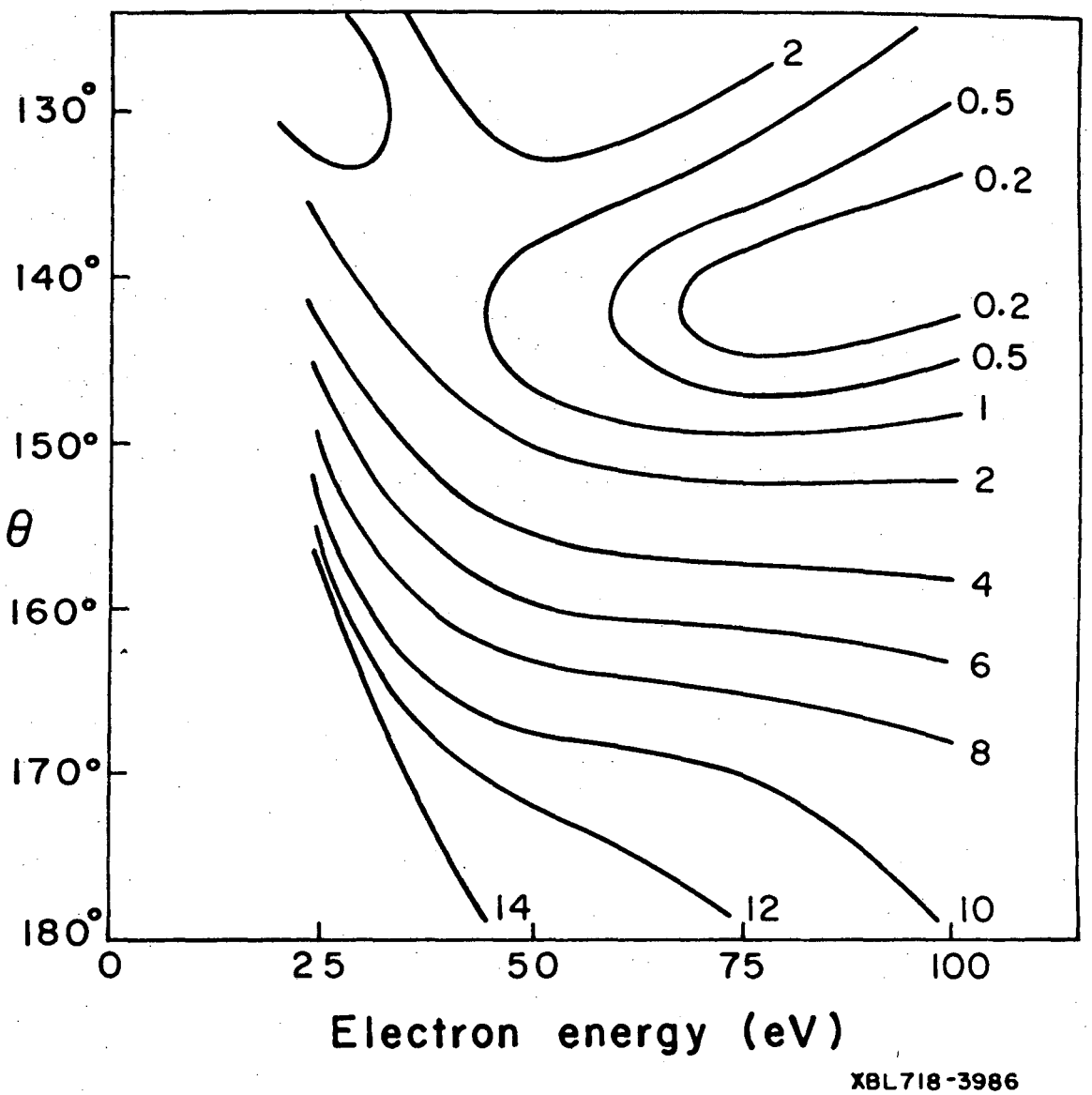
130°
140°
150°
θ
160°
170°
180°
0
25
50
75
100
Electron energy (eV)
2
0.5
0.2
0.2
0.5
1
2
4
6
8
10
12
14
XBL718-3986

Fig. 2b

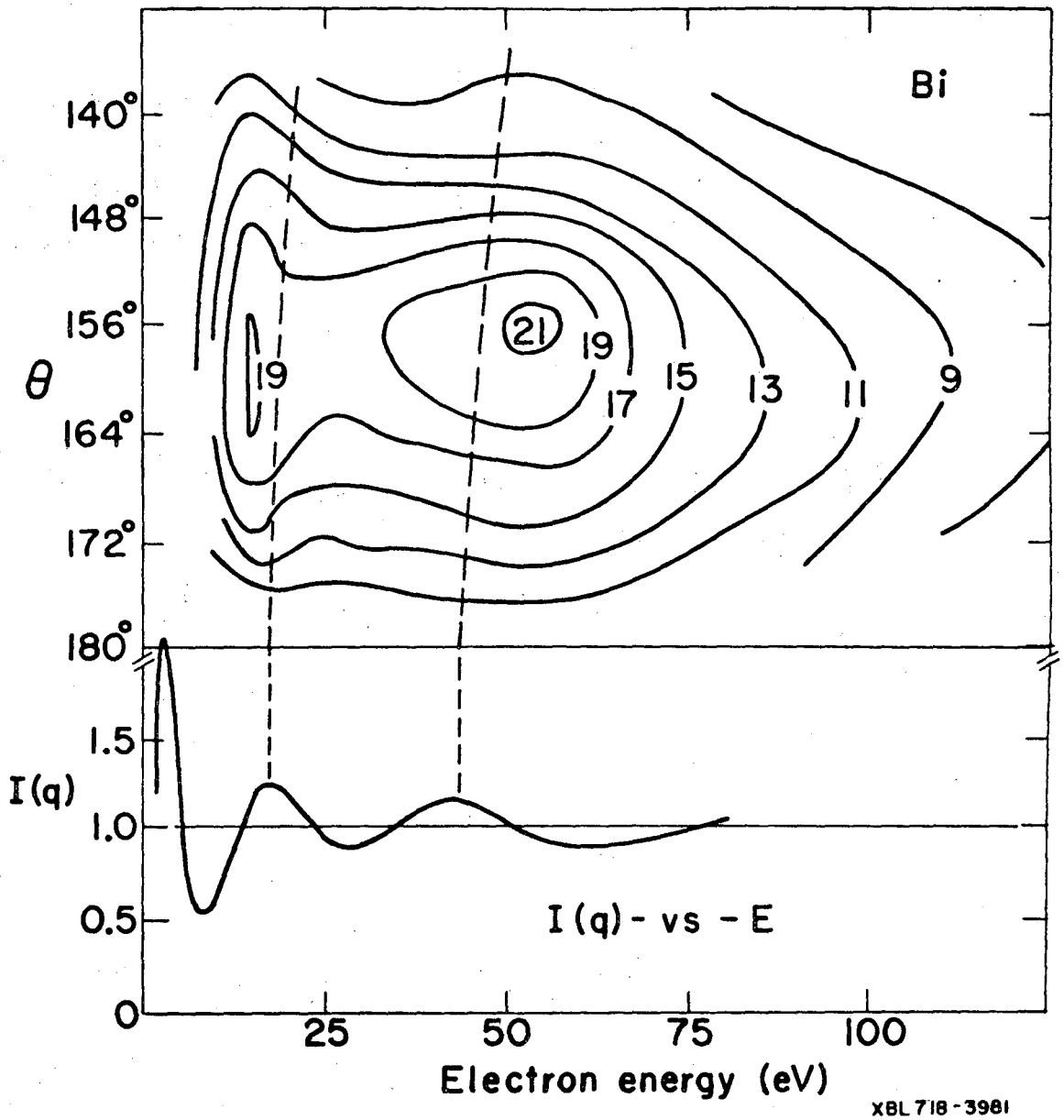
Bi
140°
148°
156°
164°
172°
180°
θ
21
19
19
17
15
13
11
9
1.5
1.0
0.5
0
I(q)
I(q) - vs - E
25
50
75
100
Electron energy (eV)
XBL 718-3981

Fig. 3

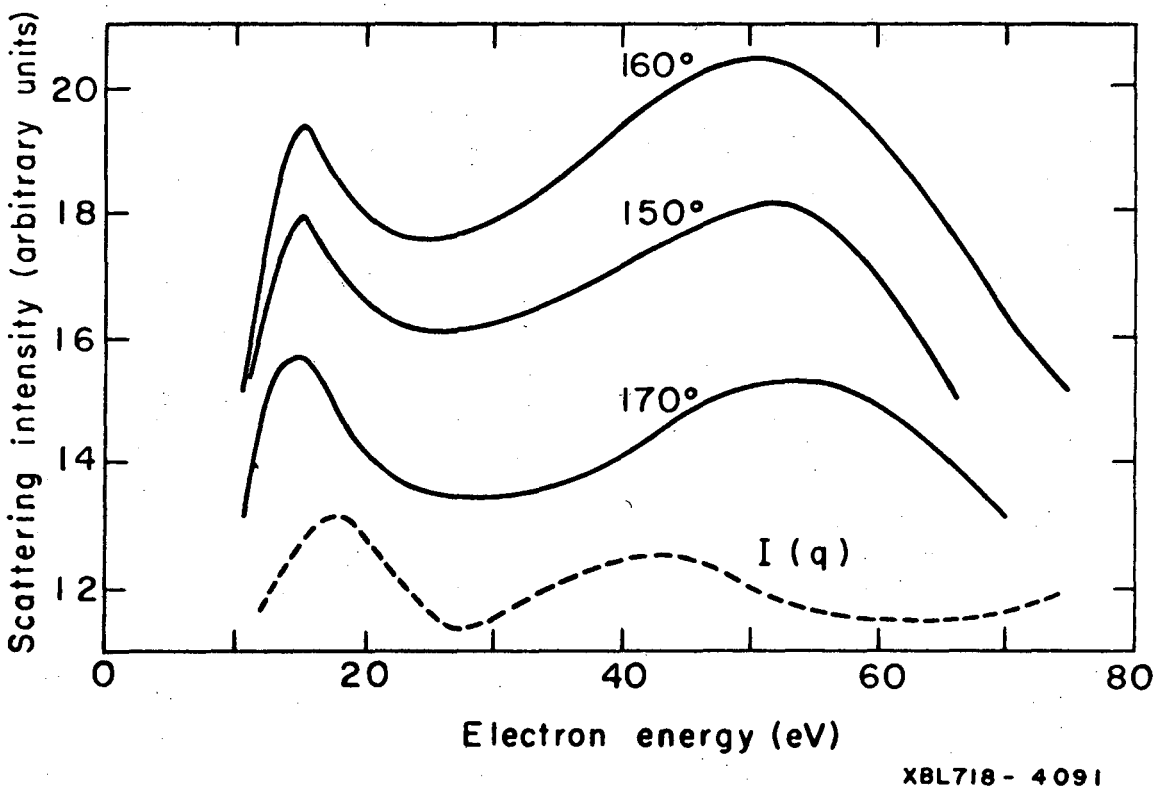
Scattering intensity (arbitrary units)
20
18
16
14
12
160°
150°
170°
I (q)
0
20
40
60
80
Electron energy (eV)
XBL718 - 4091

Fig. 4

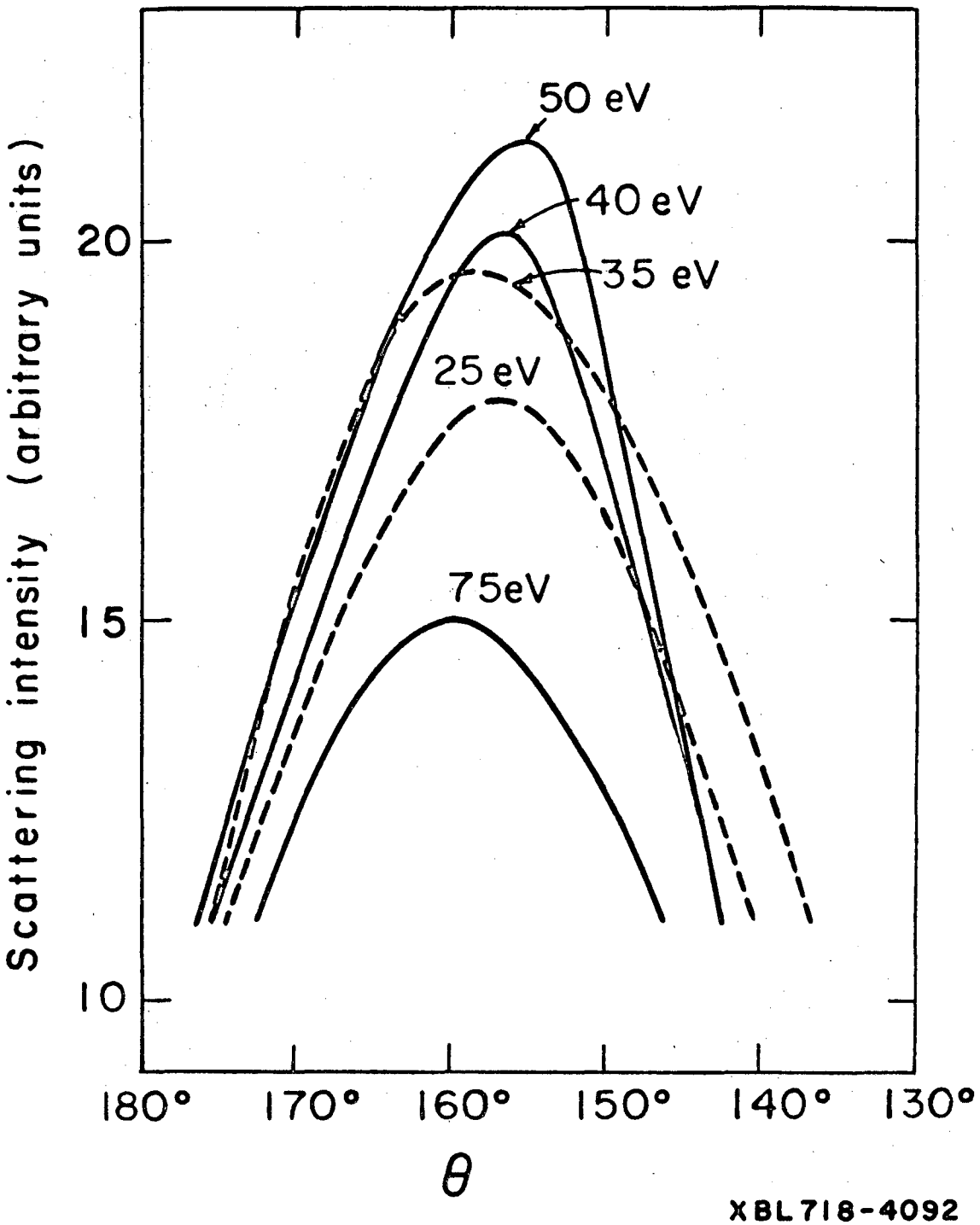
50 eV
40 eV
35 eV
25 eV
75eV
Scattering intensity (arbitrary units)
20
15
10
180°
170°
160°
150°
140°
130°
θ
XBL718-4092

Fig. 5

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