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Low Energy Electron Diffraction Studies of Liquid Lead, Bismuth, and Tin Surfaces

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Abstract

The intensities of elastically scattered low energy electrons from liquid lead, bismuth and tin surfaces were measured as a function of scattering angle and electron energy. Contour maps were constructed which display all three variables simultaneously. The intensity distribution appears to be due to uncorrelated atom scattering and thus gives directly the low energy electron-atomic scattering factor. Intensity fluctuations due to the radial distribution function in the liquid surface could not be detected. Several scattering processes are discussed which could all increase the overall background intensity and would render the intensity changes which are due to the liquid structure undetectable.

Introduction

In studies of low energy electron diffraction (LEED), the electrons incident on the single crystal surface are scattered predominantly by the surface layer or the first few atomic layers. Just as it is useful to determine the structure of solid surfaces, low energy electron diffraction might also be employed to obtain information about the structure of liquid surfaces. It is well known from studies by x-ray diffraction,[1] neutron diffraction,[2] and high energy electron diffraction[3] that the long-range order which is characteristic of solids is absent in the liquid state. Our surface melting studies[4] using LEED have clearly indicated the loss of long-range order at the bulk melting point. The spot pattern disappears and the broad intensity fluctuation which appears in the background indicate the changed distribution of elastically scattered electrons from liquid surfaces. It was the purpose of this investigation to look at the liquid surfaces by low energy electron diffraction and from the intensity of the background learn as much as possible about the structure and the scattering properties of liquid surfaces. From studies of the scattered intensity of neutrons, x-rays and high energy electrons as a function of the scattering angle, density fluctuations in the liquid can usually be extracted. From the analysis of these data the interatomic distance and the coordination number in the liquid are computed. It was hoped that from similar studies using low energy electron diffraction one can obtain the radial distribution in liquid surfaces. We have found, however, that low energy electron diffraction data from liquid surfaces do not yield the radial distribution function. The intensity fluctuations which were detectable in the low energy range

(<150 eV) were due dominantly to single atom elastic scattering which allows the experimental determination of the atomic scattering factor.

Experimental

Low energy electron diffraction unit of the post-acceleration type was used in these studies. Background pressures of the order of 10^{-9} torr were obtained in all of the studies of liquid surfaces. The starting materials were ultra-high purity single crystals of lead, bismuth and tin, which were used as cylinders or discs of various diameters described previously.[4,5] The samples were supported in crucible materials which appeared to show no chemical reaction with the solid or the molten phases. The experimental procedure was similar to that used in our surface melting studies which were described previously.[4,5] The half-wave A.C. resistance heating was used in order to avoid interference between the heating current and the incident electron beam. The circuit was designed in such a manner that only during the half-cycle while no current was flowing through the sample was the diffraction pattern monitored.

When the crystal was completely melted and the temperature was about 5° above the bulk melting point the experiment was commenced. Photographic and/or visual observations were made of the diffraction screen; then the telephotometer was focused on the diffraction screen. The three-grid energy analyzer system has been adjusted to minimize the through penetration of the inelastically scattered electrons in order to reduce the inelastic contribution to the total scattered intensity detectable on the fluorescent screen. The output of the telephotometer was plotted on the ordinate of an x-y recorder while the electron energy was plotted on the abscissa. This way, the plot of screen intensity as

a function of beam voltage could be obtained as the voltage is scanned. Due to the low screen intensity (the electrons scattered by the liquid surface are more evenly distributed than those scattered by solid surfaces) a large aperture optical fiber and high sensitivity spot photometer setting had to be used in these studies. The voltage was scanned in the range of 0-125 electron volts. After a voltage scan the fiber optics was focused at a new position on the screen, generally in about 5° to 6° intervals along the radius from the electron gun to the edge of the screen, and the electron energy was scanned again. As a result, a set of 6 or 7 scans were obtained corresponding to 6 or 7 different screen angles. Since the intensity variations in the scattered intensity for molten metal surfaces proved to be very gradual, this was considered to be sufficient to map the entire screen intensity profile. The visual and photographic evidence indicated that the intensity fluctuation had radial symmetry about the electron gun axis. Tests made by rocking the crucible to cause the liquid surfaces to move convinced us that our results were independent of the orientation of the liquid surface.

The cleanliness of the molten surface is most readily checked by cooling the crystal below its freezing point and observing the resultant diffraction pattern of the crystal surface. The recrystalized surfaces always displayed sharp diffraction patterns and thus, the liquid surfaces were considered to be clean.

Results

The experimental results obtained from the voltage scans at different scattering angles were normalized to constant electron emission in order to eliminate one of the experimental variables from the experimental curves.

The most convenient presentation of the measured intensity at different scattering angles and beam voltages from liquid surfaces is in the form of contour maps. The ordinate is taken as the screen angle, ϕ, with respect to the electron gun which is in the center of the screen (surface normal). The abscissa is the beam voltage and the contours are normalized intensities in arbitrary units. Figures 1, 2, and 3 show results from molten lead, bismuth and tin surfaces respectively. The intensity contours connect those scattering angle and beam voltage values which are characterized by uniform intensity. To convert the screen angle, ϕ, to a more usual angular variable let the scattering angle, θ, be equal to $\theta = 180° - \phi$ where $\phi = 0$ refers to the exact back-scattering or 180° scattering. The intensity units, even though arbitrary, are directly comparable on all three contour maps (Figures 1, 2 and 3) since the scales were made using the same telephotometer settings and same sensitivity of the electron optics. The dotted line in the figures refers to the locus of points in our coordinate system for the first intensity maximum characteristic of high energy electron diffraction studies of molten metals.[6] Figure 4 is an intensity map calculated from x-ray data by Kaplow[7] on liquid lead. Similar results were obtained by Richter, et al.[3] using high energy electron diffraction. Their data was extrapolated to our region of low energies; the dotted line connects the points where the first maximum should appear. It is readily apparent that none of the experimental curves show features comparable with this calculated curve. Thus, the intensity fluctuations which we have detected cannot be used to calculate the radial distribution function from liquid surfaces. The reasons for the absence of any indication of density fluctuations in surfaces in the scattered low energy

electron beam intensity will be discussed below. It is, of course, possible that the surfaces of liquids are characterized by very different distribution functions then bulk liquids and interference between the different scattering distributions (surface and bulk) may mask the radial distribution function intensity fluctuations. However, we consider this improbable.

It is of interest to analyze the intensities which are obtained from the three liquid surfaces which we have studied in more detail. For lead, there are no sharp features but rather a general intensity maximum about 55 electron volts at a screen angle of roughly $\phi = 0°$ with a fairly uniformly decreasing intensity toward large angles and toward lower and higher energies. There is a small ridge starting at large angles and low energies and sloping towards the primary maximum. For bismuth we have well-defined ridges running uniformly between $\phi = 20° - 24°$ at all energies and at 20 and 55 electron volts for all angles. The intersection of these intensity lines produces peaks about 20° and 20 volts, and 24° at 55 volts with a saddle point at 22° and 25 volts. At higher energies, about 60eV, the pattern shows uniform decrease of intensity away from the central maximum very similar to the behavior for lead. For tin, (figure 3) the major features are the high peak at about 65eV and $\phi = 0°$. There is a fairly sharp depression at 25eV from $\phi = 33°$ upward. In addition, there is a slight ridge running from $\phi > 48°$ and 35 electron volts diagonally toward a central maximum at about 20° and 55 eV. A large shallow depression is found at $\phi = 48°$ for all energies larger than 80 eV.

In interpreting these results, several factors must be kept in mind

which limit the accuracy of the experiments. 1) The sample obscures part of the screen near $\phi = 0°$ incidence. This was especially troublesome for the large lead discs which covered $\pm$ 8° solid angle about the surface normal. 2) The screen only extends to 48° from the surface normal so intensity changes at larger angles could not be observed with our instrument. The use of Faraday collectors should be considered to extend these measurements to larger angles. 3) Inhomogeneities in magnetic fields might slightly modify the distribution of scattered electrons. 4) Due to low screen intensities one must use large photometer apertures and high photomultiplier gain which leads to noise and loss of precision. 5) The possibility of some degree of surface contamination can never be ruled out on liquid surfaces. Diffusion rates of impurities could be many orders of magnitude faster in liquids than in solids. Low solubility impurities might float to the surface of the liquid and obscure some of the scattered intensity features.

Discussion

The elastically scattered electrons from liquid surfaces should show a distribution which reflects two scattering mechanisms;[8] 1) Uncorrelated scattering from individual atoms in the liquid surface, and 2) Scattering which is modulated by the density fluctuations in the liquid surface. The latter should give rise to intensity fluctuations which can be used to obtain the radial distribution function.

Figure 5 gives the x-ray intensities obtained by liquid lead at 327.4°C as a function of scattering angle, $\frac{S}{4\pi} = \frac{\sin\theta}{\lambda}$, which are mainly the result of these two scattering mechanisms. It should be noted that the peak intensities are, at best, twice the background intensity.

Perhaps the most significant result of our LEED studies of liquid surfaces would be if we could associate the observed intensity distribution as solely due to single atom scattering mechanism. In that case the data directly gives the atomic scattering factor, f. This parameter enters into calculations of surface structure from the diffracted beam intensities and its experimental determination would eliminate the uncertainties inherent in its theoretical evaluation using an assumed atomic potential. It appears from the experimental data (Figures 1, 2 and 3) that intensity fluctuations which would reflect the density changes in the liquid surface are missing from our intensity distribution.

Let us consider additional scatterings mechanisms which could contribute to the intensities observed by scattering of low energy electrons from liquid surfaces. a) Inelastic electrons which lost small energy (< 2 eV) may penetrate the repelling grids and contribute uniformly to the background intensity thereby diminishing the magnitude of the intensity fluctuation. b) Multiple scattering effects which are due to further interactions between the scattered electron beams and c) thermal diffuse scattering which attenuates the intensities of the diffraction features from liquid surfaces due to increased vibrations of atoms in the disordered surface.

Inelastic contributions to the scattered intensity would uniformly increase the background and may mask small intensity fluctuations. Thus, this term would not be expected to change the intensity distributions due to 1) and/or 2). The effect of multiple scattering is difficult to assess. It might introduce additional intensity fluctuations which would be superposed on the single scattering distribution so that single and

multiple scattering contributions could not be separated. Thermal diffuse scattering has been discussed by Webb et al. in some detail.[9] Since this term is proportional to the atomic scattering factor and to the Debye-Waller factor, it should not change the intensity distribution markedly.[5]

Therefore, it may be concluded that the intensity distribution of the low energy electrons scattered by lead, bismuth and tin liquid surfaces gives us directly the low energy electron atomic scattering factor for which single and multiple scattering contributions are indistinguishable.

Although it is somewhat disappointing that intensity fluctuations due to the radial distribution function in the liquid surface could not be detected by low energy electron diffraction (LEED) (in view of the easy detectability of this effect in the bulk liquid by high energy electron diffraction (HEED), x-ray and neutron diffraction) the absence of these features can easily be rationalized. All three effects, a), b), and c), which were mentioned above would be instrumental in reducing the intensity changes by increasing appreciably the background intensity. It should be remembered that the peak intensities are never more than a factor of two higher than the background intensity in all of these experiments with bulk liquids near the melting point. There may be an additional reason for masking the scattering due to the liquid "surface structure" (i.e., correlated disorder[9]). Due to the low penetration depth of the electron beam in LEED experiments the number of atoms which contribute to coherent scattering is at least two orders of magnitude smaller than in HEED experiments. An estimate of the number of atoms which can contribute

to coherent scattering as a function of electron energy is given in the appendix.

There is a great deal of evidence that the low energy electron atomic scattering factor can also be obtained by monitoring the background intensity from disordered solid surfaces in LEED experiments.[10][11] However, it should be harder to interpret these experiments and to extract the atomic scattering factor from the intensity data. Due to the crystal periodicity below the disordered surface layer there are additional scattering mechanisms which would strongly modulate the background intensity. These are diffraction effects and Kikuchi scattering. Therefore, it appears to be of advantage to use liquid surfaces to determine the atomic scattering factor by direct measurement of the intensity as a function of scattering angle at different incident beam voltages.

The three dimensional contour maps employed here (Figures 1, 2 and 3) should be useful to record low energy electron diffraction data and to correlate trends as a function of all three variables, electron energy, scattering angle and intensity, simultaneously.

Appendix

There is an upper limit to the area of the crystal surface which receives coherent radiation from a finite electron source.[12] An estimate of the coherency of incident electrons can be made for the typical LEED electron optics for which β_s, the half angle indeterminancy of the source is $\beta_s = 10^{-3}$ radians. The coherence length, ΔX, in the surface which receives coherent radiation of energy E and energy speed ΔE is given by

$$\Delta X = \frac{\lambda}{2(1 + \frac{\Delta E}{E})\beta_s} \qquad \text{(A1)}$$

which reduces for electrons in LEED or HEED TO

$$\Delta X \simeq \left(\frac{150.4}{eV}\right)^{1/2} \frac{1}{2\beta_s} \qquad \text{(A2)}$$

since $\lambda = \left(150/_{eV}\right)^{1/2}$ and $\Delta E < 1eV$ so that $\frac{\Delta E}{E} << 1$. The number of atoms contained within the "coherence area," N, is given by

$$N = \frac{\pi (\Delta X)^2}{\pi r^2} = \frac{150.4}{4eV\beta_s^2} \frac{1}{r^2} \qquad \text{(A3)}$$

where r is the atomic radius. In order to estimate the penetration depth, L, of electrons as a function of electron energy we use the data given by Heidenreich[13] which suggests $L \sim (eV)^n$ where n = 2. The following formula is taken as a good estimate,

$$L \text{ (penetration in units of atomic layers)} = 2 + (^{eV}/_{150})^2 \qquad \text{(A4)}$$

although n = 1.5 to 1.9 is frequently chosen. Using (A3) and (A4) and the values $r \sim 2\text{Å}$ and $\beta_s \sim 10^{-3}$ radian, we can estimate the total number of atoms N_T, in the scattering volume $N_T = NL$ as a function of electron energy. We obtain the following values,

eV	15	45	150	450	1.5×10^4	4.5×10^4	1.5×10^5
N_T	5×10^5	7×10^5	2×10^6	7×10^6	2×10^8	7×10^8	2×10^9

Thus, for LEED experiments $N_T \sim 10^6$ while for HEED, $N_T \simeq 10^9$. Since the intensity varies as N_T^2 it is expected that HEED should be more sensitive to small degree of ordering than LEED.

Acknowledgement

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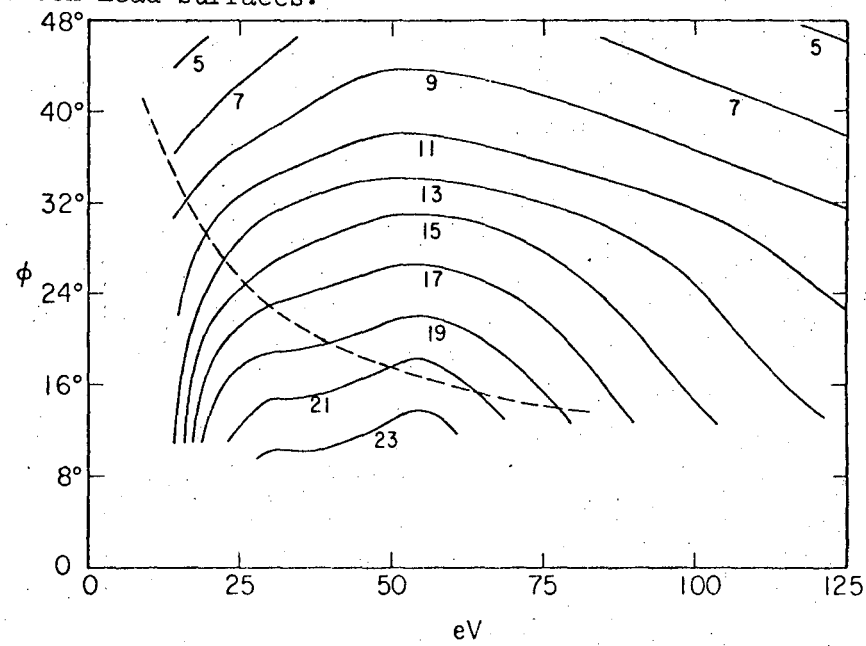
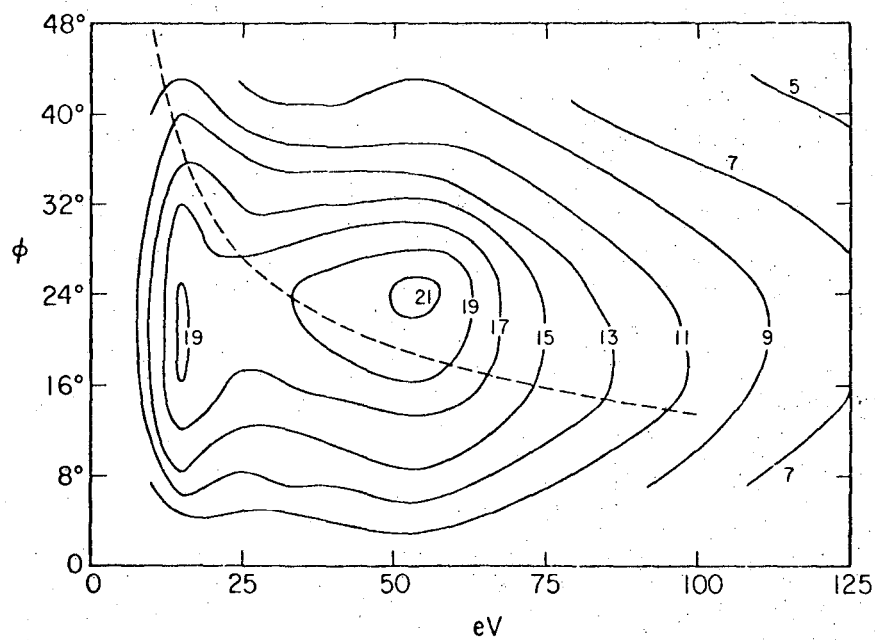
Figure 1. Low energy electron diffraction intensity contours as a function of screen angle, ϕ , and beam voltage, eV, from molten lead surfaces.

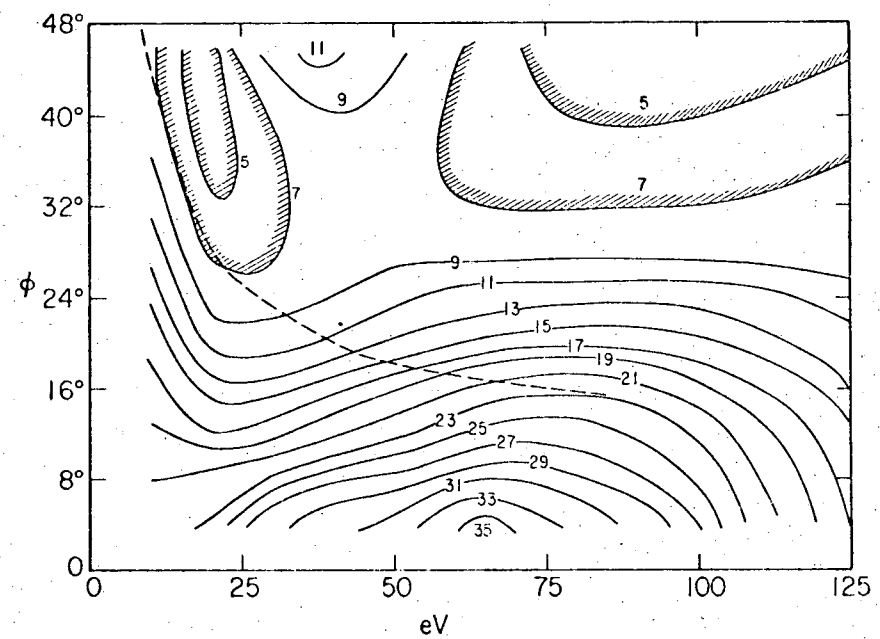


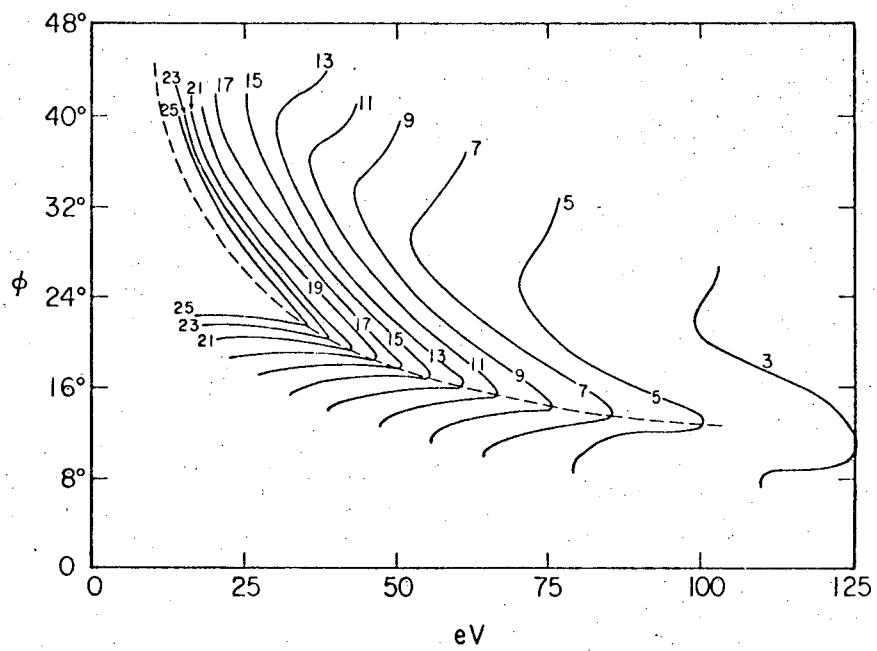


XBL 696-637

Figure 2. Low energy electron diffraction intensity contours as a function of screen angle, ϕ , and beam voltage, eV, from molten bismuth surfaces.

Figure 3. Low energy electron diffraction intensity contours as a function of screen angle, ϕ, and beam voltage, eV, from molten tin surfaces.





XBL 696-640

Figure 4. Predicted intensity contours as a function of screen angle, ϕ, and beam voltage, eV, from LEED and x-ray diffraction studies of molten lead.

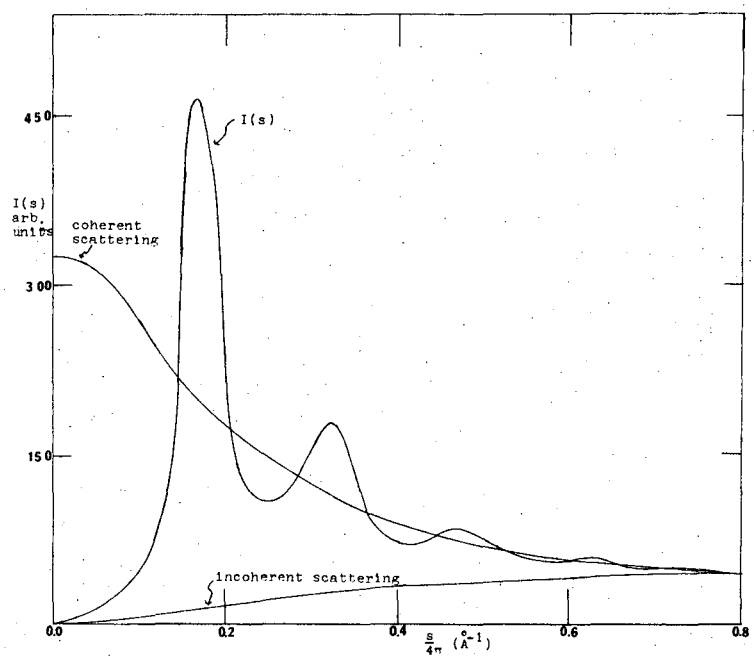


Figure 5. X-ray intensities obtained from molten lead at 327.4°C as a function of the scattering angle, $S/4\pi = \frac{\sin\theta}{\lambda}$.

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