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Low Energy Electron Diffraction Studies of Surface Melting and Freezing of Lead, Bismuth, and Tin Single Crystal Surfaces.

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Abstract

The surface structures of the (111), (100) and (110) faces of lead, the (0001), $(01\bar{1}2)$ faces of bismuth and the (110) face of tin single crystals were monitored up to the melting temperatures and during melting by low energy electron diffraction. Measurements of the surface Debye-Waller factor from the different lead and bismuth surfaces indicated mean square displacements of surface atoms perpendicular to the surface plane, $\langle u_{\perp}^2 \rangle_{surf}$, which were much larger than the bulk mean square displacements at the melting points as predicted by the Lindemann melting model. However, the diffraction features have persisted in all of the crystal faces up to the bulk melting points of these solids. These results indicate that the surfaces remain ordered up to the bulk melting point and that the crystal surface plays an all important role in nucleating or initiating melting. Several experimental melting studies and pertinent melting models have also been discussed.

The surface orientation of lead and bismuth crystals were monitored during freezing and growth from the melts. The dominant surface structures which formed upon freezing were dependent on the cooling rate. Slow rates ($\leq 0.5°C/sec$) favored the formation of the Pb(111) and Bi($01\bar{1}2$) surfaces while during rapid cooling ($> 0.5°C/sec$) the Pb(100) and Bi(0001) crystal faces have predominated.

Introduction

The thermodynamic parameters which characterize the melting process (ΔH_{fusion}, ΔS_{fusion}, ΔV_{fusion}, etc.) have been well established for most monatomic and diatomic solids. Detailed discussions of the thermodynamics of melting are available[1,2] along with recent improvements of the thermodynamic data.[1] The kinetics of melting however, that is the mechanism by which the melting interface moves into the bulk of the solid, has been investigated to a much lesser extent. Although several theories of melting have been proposed,[3,4,5,6] the experimental information which would allow one to develop a realistic mechanism of melting has been accumulating only in the past several years. There are at least two melting theories[7,8] which indicate that the surface properties are important in understanding the mechanistic aspects of the melting process. Recent kinetic studies of superheating[9,10] have shown that surfaces play an important role in initiating or nucleating melting. Studies in this laboratory,[11,12,13] and in others,[14,15] of the mean square displacement of surface atoms by measuring the temperature dependence of the low energy electron diffraction beam intensities have shown that for several monatomic face centered cubic metals the mean square displacement of atoms in the surface is appreciably larger than the mean square displacement of atoms in the bulk. Since there is at least one model of melting[16,17] which indicates that the mean square displacement plays an important role in determining the melting temperatures, these results indicate that surfaces may disorder(i.e. lose their long range order) at temperatures below the bulk melting point.

In order to explore the importance of surfaces in the melting process and to investigate whether the surfaces premelt (that is, melt at a temperature below the bulk melting point) we undertook low energy electron diffraction studies to monitor the surface structure up to the melting point, and the order-disorder phenonmena on the surface at the melting point. We have chosen in these studies lead, bismuth, and tin single crystal surfaces. These metals were particularly suitable for low energy electron diffraction studies which have to be carried out in ultra high vacuum since they have very low vapor pressure ($< 10^{-8}$ torr) at their respective melting points. There are, however, important differences in many physical-chemical properties of these materials. They have different crystal structures. Lead and tin, like most solids, expand upon melting. Bismuth undergoes a negative volume change on melting; it contracts. Thus, we can study the effect, if any, of these properties on the melting and freezing kinetics. We have studied the melting of the (111), (100) and (110) crystal faces of lead, the (0001) and $(01\bar{1}2)$ faces of bismuth and the (110) crystal face of tin. We have found that the surface structures remained unchanged and long range order in these surfaces was maintained up to their respective bulk melting temperatures for all the crystal faces studied. From the results of our studies and from experimental studies of melting kinetics of different types on other materials by several investigators, a more complete physical picture of melting seems to emerge. These data are summarized in the hope that it will foster the development of a more rigorous melting theory. A strong correlation between the rates of freezing and the surface orientation of the growing crystallites of lead and bismuth has also been established.

Experimental

A modified low energy electron diffraction unit of the post-acceleration type was used in these studies. Ambient pressures of 2-5 x 10^{-10} torr were obtained and maintained during most of the melting experiments. Single crystals of the highest available purity were used in these studies. Spectroscopic analysis has shown copper, iron and tin impurities in 10 to 10^3 ppm concentrations to be present in lead while impurities in the 1-10 ppm range were reported in bismuth or tin. The crystals were oriented by X-ray diffraction, and spark-cut. Chemical etchings of the single crystal surfaces were carried out using glacial acetic acid and 30% hydrogen peroxide (2:1) for lead, concentrated hydrochloric acid followed by a mixture of nitric acid, glacial acetic acid and glycerin (1:3:5) for tin, and using concentrated nitric acid for bismuth surfaces.[18] The samples were used in the form of cylinders (5 x 7 mm) or discs (4 x 20 mm). The holders which were used to support the single crystal samples were high purity iron for bismuth and lead and high purity molybdenum for tin. The crucibles were machined to fit each crystal snugly to insure good thermal contact and to prevent the sample from moving during ion bombardment. The diffraction chamber was rotated by 90° (see Fig. 1a) to prevent loss of molten samples. The diffraction spot intensities were measured by monitoring the fluorescent screen intensity through the mirror as a function of the experimental variables such as temperature, electron beam energy, and scattering angle, using a photometer with fiber optics. The crystals were in general heated to their respective bulk melting points in the holders which were heated resistively. In some of the melting studies

the crystal was heated near to its melting point in this manner. Further heating was accomplished by thermal imaging a tungsten filament onto the crystal surface as shown in Fig. 1b. This way, variable temperature gradients from the surface of the samples to the bottom part or across the surface could be introduced and maintained. Since the bulk melting points of the studied solids are fairly low (Tm for lead 327°C, Tm for bismuth is 271°C and Tm for tin is 232°C), heating resistively or by thermal imaging could be adequately controlled to within ± 1 degree. The temperature was measured continously during the course of the experiments using a thermocouple attached to the crucibles. The melting point of the samples provided an excellent means of calibration of the thermocouple response. In order to avoid interference with the visual monitoring of the diffraction pattern by the perturbing magnetic fields which are introduced by the heating current, a half-wave a.c. current was used for heating. The circuit was designed in such a way that the diffraction pattern was viewed in the off-cycle periods.[18] The intensity of the diffraction spots at any temperature and incident electron energy depends on the surface Debye-Waller factor, 2W, which is given by[11]

$$I_{hkl} = \left| F_{hkl} \right|^2 e^{-2W} \tag{1}$$

where

$$-2W = \frac{12Nh^2}{Mk} \cdot \frac{\cos^2\phi}{\lambda^2} \frac{T}{\Theta_D^{\,2}} \tag{2}$$

where M is the atomic weight, λ is the wave length, ϕ is the scattering angle and Θ_D is the Debye temperature. The other constants have their usual meaning. Thus, the intensity of a given diffraction spot decreases

exponentially with increasing temperature. The larger the atomic weight and the Debye temperature, the higher the temperature at which the diffraction spots are still distinguishable from the background. Conversely, the intensity should diminish with increasing electron energy (i.e. shorter wave length) at a given temperature. LEED experiments indicate that equations 1 and 2 are obeyed in general and diffraction spots at lower electron energies persist to higher temperatures. One may use the product, $M\Theta_D^2$, as a figure of merit, the magnitude of which determines the approximate temperature range in which the strongest diffraction beams (generally the (00) and (10) reflections) become indistinguishable from the background at the lowest electron energies (20-35 eV). Our experiments indicated that for lead, bismuth, and tin, diffraction beams could be monitored up to the bulk melting point.

The experimental criterion used to ascertain melting was the loss of the diffraction features, i.e., the disappearance of the diffraction spots which are due to long range order in the crystal surfaces. If the surface remains ordered, the diffraction spots should be visible right up to the melting point or to the temperature at which the loss of long range order occurs. It should be noted however, that the concentration of disordered surface atoms could be as high as 5-10% of the total surface concentration before there is an experimentally detectable decrease in the LEED spot intensities.[18] The low energy electrons which were scattered from the liquid metal surfaces gave rise to broad intensity fluctuations which could be monitored using the fluorescent screen (see Fig. 3a and 3b). The low energy electron diffraction features which were characteristic of the liquid metal surfaces will be discussed in a subsequent paper.

Results

A. Measurements of the mean square displacements of surface atoms.

The mean square displacements of surface atoms perpendicular to the surface plane, $\langle u_\perp^2 \rangle$, in the (111) and (110) surfaces of lead, and in the (0001) and $(01\bar{1}2)$ surfaces of bismuth were measured by monitoring the intensity of the (00)-reflection as a function of temperature. From the slope, the effective Debye temperature, Θ_D^{eff} at a given beam voltage, V, could be determined from the formula[18]

$$\frac{d \log(I_{oo} - I_B)}{dT} = \frac{KV \cos^2\phi}{M(\Theta_D^{eff})^2} \qquad (3)$$

where K is a constant (k = 66.6 g°K/mole eV) and I_B is the background intensity.[11,18] The same experiment was repeated at different beam voltages and the results are given in Fig. 2 for lead and in Fig. 3 for bismuth surfaces. The values of Θ_D^{eff} which were calculated from equation 3 are plotted as a function of electron energy. The extrapolated value at zero electron energy is taken as the surface Debye temperature. The surface mean square displacements can be computed by using the equation

$$\langle u_\perp^2 \rangle_{surf} = \frac{3Kh^2}{Mk} \frac{T}{\Theta_{D,\ surf}^2} \qquad (4)$$

At higher electron energies, when a larger fraction of the electrons penetrate into the bulk, the calculated Debye temperature approaches the bulk value which may also be determined from independent measurements. The beam voltage at which the bulk value is reached depends on the

penetration depth of the electrons which changes from material to material, crystal face to crystal face, and is also a function of the angle of incidence.[11,12,18] This is the reason for the different slopes of the Θ_D^{eff} vs. eV curves which are shown in Figs. 2 and 3. Using equation 4, the root mean square displacements of surface atoms of lead and bismuth can be calculated to be $\langle u_\perp^2 \rangle_{surf}^{\frac{1}{2}}$ for Pb(111) = 0.298Å; for Pb(110) = 0.395Å; for Bi(0001) and $(01\bar{1}2)$ = 0.302Å.

There is at least one melting theory, the Lindemann theory,[16,17] which predicts a linear correlation between the mean square displacement and the melting point. According to this model melting commences, i.e., the crystal lattice collapses when the vibrational amplitude of atoms in the solid reaches a critical value which is a certain fraction of the interatomic distance. Although Lindemann has only proposed an empirical relationship between the melting point and the Einstein frequency,[16] several alterations have been made in the theory to increase the accuracy of its "predictions." It is probably best to consider it in the form which was proposed by Gilvarry,[17]

$$\Theta_D = \text{const}\left(\frac{T_m}{Ma^{2/3}}\right)^{1/2} \qquad (5)$$

where M is the atomic weight and a is the atomic volume. The surface Debye temperatures which were obtained experimentally are, in fact, larger than the predicted bulk Debye temperatures at the melting point--as predicted by the Lindemann model. Thus, according to this melting model the large experimental surface mean square displacement indicate that surface melting could occur below the bulk melting point.

B. Surface melting studies.

In these studies, the diffraction patterns of the different crystal faces of lead, bismuth, and tin were monitored visually and by the photometer as a function of temperature up to and at the melting temperature. The diffraction spot intensities decreased monatomically according to the temperature dependence predicted by the Debye-Waller factor but were always detectable until the bulk melting point was reached. In every experiment the diffraction pattern remained intact until, at the bulk melting point, the molten interface reached that region of the surface where the electron beam was focused. Then, the diffraction spots disappeared. In one experiment using a large Pb disc, a temperature gradient was introduced along the surface such that melting commenced near one edge of the disc and the melting front proceeded across the surface very slowly (it took about 20 minutes to melt the entire disc). By suitable manipulation of the trimming magnets, the electron beam was focused near the hottest part of the crystal and as the pattern from this area disappeared due to melting the beam was moved to an adjacent still solid portion and diffraction pattern was again obtained until that region melted and so forth. In a particular experiment with Bi, heating was performed from the bottom. Since the solid is less dense than the liquid, the surface solid remained intact and floated on the molten bismuth beneath. As the crystal melted completely the last solid portion would float around on the liquid and the diffraction spots would move correspondingly.[18]

The melting of the Pb(110) surface was studied with particular care since it is the lowest density and the highest surface free energy surface of the three lead crystal faces studied. In fact, once melted,

the (110) orientation has never appeared on the recrystallized lead samples. Nevertheless, the (110) surface proved to be ordered and stable to the bulk melting point of lead just like the (111) and (100) crystal faces.

Lead has a face centered cubic structure while bismuth has a rhombic crystal structure. The bismuth lattice is similar to a simple cubic lattice which is slightly distorted. The Bi(0001) face corresponds to a pseudo-cubic (111) orientation while the Bi($01\bar{1}2$) face is a pseudo-cubic (100) crystal face. Lead, unlike bismuth expands on melting. It appears that the surface melting characteristics are not influenced by the differences in crystal structure or volume change during fusion.

Freezing the molten lead and bismuth samples after a melting experiment by cooling the crucible below the freezing point of the metals usually produced crystallites with sharp, high intensity diffraction features. This was taken as convincing evidence that the metal surfaces were free of contamination during the melting experiments.

The surface melting experiments with Sn(110) surfaces were more difficult to perform. In every case a surface structure has formed on this face. This structure agrees with the (3 x 1) surface structure reported by Jackson and Hooker[19] for slow epitaxial deposition of tin on Nb(110) surfaces. Surface contamination problems were certainly serious in the melting studies with Sn(110) surfaces. Frequently, upon heating these crystals to > 70°C there was a rapid irreversible decrease of the diffraction spot intensities. The sharp high intensity diffraction pattern could only be regenerated after extensive ion bombardment. Due to this deterioration of the diffracted beam intensities from crystals which have not previously been melted the diffraction spots were only

visible to within 6-8° of the melting point. The crystal surfaces, however, which formed after recrystallizing the molten tin visible to the bulk melting point and generally behaved very much like the lead and bismuth surfaces previously described. The (110) orientation could never be found on the regrown crystal surfaces. Unfortunately, none of the recrystallized surfaces could be readily indexed as any low index face of white tin. Thus, they may be a) ordered impurity structures or b) surface structures on low index tin surfaces. A more detailed discussion of the different tin surface orientations which formed after recrystallization of molten tin is given elsewhere.[18]

In summary, the three crystal faces of lead, [(111) (100) and (110)] two different crystal faces of bismuth, [(0001), $(01\bar{1}2)$] were studied and showed no premelting. They remained stable to the bulk melting point and they melted spontaneously at that temperature. Contamination of lead and bismuth surfaces could be completely avoided. Formation of surface structure and contamination problems made the melting studies with tin(110) surface difficult to perform.

C. Studies of Freezing of Molten Lead and Bismuth

These investigations were performed to discover the experimental parameters which influence the surface structure of recrystallized metals and their kinetics of freezing and growth. Studies of the surface structures of metal crystals during refreezing should provide a great deal of information on the mechanism of crystal growth from the melt. The molten lead and bismuth were cooled using cooling rates in the range of 2°C per second to .02°C per second. It was found that during freezing more than one crystallite formed. These crystallites were nucleated at the holder walls, as expected. Although the size of these crystallites varied, most

of them were large enough to show sharp diffraction features allowing us to monitor their orientation and surface structure. Their orientation was checked by locating the specular or (00)-spot for each prominent crystallite. For example, if a hexagonal pattern was observed from lead with a (00)-spot 11° from the direction of incidence of the electron beam that crystallite could be indexed to have its (111) axis orientated 11° with respect to the surface normal. The contraction of lead upon freezing which starts at the crucible walls tended to create craters at the surface of the crystal while conversely the expansion of bismuth upon freezing tended to create protrusions on the crystal surface.

In discussing the effect of cooling rate on surface orientation one may take the cooling rate of 0.5°C per second as a dividing line between rapid and slow freezing rates. Rapid freezing rates (> 0.5°C per second) favored the growth of the (100) surfaces of lead while slow cooling rates (< 0.5°C per second) favored the formation of the Pb(111) surfaces. For bismuth surfaces, we have obtained the following results; rapid cooling rates favored the appearance of crystallites orientated with the [(0001)] (pseudo-cubic [111]) or hexagonal axis perpendicular to the crystal surface, while slow freezing rates favored crystallites with the $[01\bar{1}2]$ (pseudo-cubic [100]) axis oriented perpendicular to the crystal surface.

It should be mentioned that undercooling of liquid lead of the order of 8°, were frequently observed during studies of the recrystallization of lead. However, bismuth did not show undercooling in any of the crystal growth experiments.

Discussion

Low energy electron diffraction studies of the melting of low index lead, bismuth, and tin single crystal surfaces in which the disappearance of the diffraction pattern characteristic of long range order was taken as the sign of melting indicated no surface premelting. The different surfaces seemed to disorder at the respective bulk melting temperatures. Although bismuth undergoes negative volume change upon melting and has a crystal structure different from that of lead the melting behavior of its surfaces were similar to that of lead surfaces.

The low energy electron diffraction pattern is insensitive to the presence of disordered atoms on the surfaces as long as their concentration is only a few percent of the total surface concentration.[20] Thus the presence of a LEED pattern from the different surfaces which suggests the dominance of long range order on the surface up to the bulk melting point does not rule out the presence of disordered atoms in few atom percent surface concentrations. There are several additional experimental observations accumulated in recent years which shed light on the mechanism of melting. Turnbull, et al,[9,21] showed that bulk SiO_2 and P_2O_5 crystals could be superheated by 300°C and 50°C respectively due to the slow propagation of the viscous molten interface into these solids. Melting was found to nucleate always heterogeneously at emerging dislocations or imperfections and then propagate into the bulk. In order to avoid nucleating of the melt at the surface, Käss and Magun[10] heated the inside of an ice single crystal while keeping the surface below the melting point. This way they were succesful in observing superheating. Similar results

were obtained by other investigators using gallium crystals.[22] Several experiments show that in the presence of small temperature gradients, the melting rate varies along different crystallographic directions.[22] These observations indicate that melting has to be nucleated and that the crystal surfaces appear to provide nucleation centers most efficiently. Thus, when melting occurs in the presence of a surface, a condition almost always met in melting experiments, superheating cannot be observed due to the large concentration of surface nucleation sites. Although most of the surface remains ordered up to the bulk melting point, it is likely that the nucleation sites are already present before melting commences. As soon as the liquid phase becomes thermodynamically stable, the solid-melt interface may propagate along the surface or into the bulk from these nucleation centers equally well.

A melting theory to be successful should have to explain the kinetic, thermodynamic and statistical properties of the melting phase transformation. These are (1) low index surfaces of simple monatomic solids remain chiefly ordered up to the bulk melting point, (2) superheating of solids occurs only in the absence of nucleation sites or because of the slow propagation of the melt interface, (3) nucleation of melting occurs most easily at the surface and the melt propagates into the bulk from the selected surface nucleation sites (4) X-ray, neutron and high energy electron diffraction experiments indicate that melting occurs with the loss of long range order, and (5) melting is a first order phase transition with well defined thermodynamic parameters [(ΔH_{fusion}, ΔS_{fusion}, and ΔV_{fusion})]. So far none of the melting models which have been proposed have been able to account for all of these properties. It is hoped that in the near future a judicious synthesis of the favorable features of some of these proposed models, which will be enumerated below, will produce a melting model which allows quantitative prediction of the melting characteristics of different solids.

There are several melting models which explain the kinetic properties of melting which were uncovered by recent experiments. Hillig and Turnbull[5] have proposed a melting model which allows the computation of the propagation velocity of the molten interface in a temperature gradient which is provided by superheating. Good agreement between their theory and the experiments could be reached only if they had assumed that melting occurs only at a small fraction of the surface sites at the solid-melt interface.

What is the nature of those surface sites where melting may be nucleated? None of the experimental melting studies so far have been able to identify these centers. They may be vacancies or vacancy aggregates, or disordered regions around dislocations which emerge at the surface. Stark[8] has proposed that the vacancy concentration at the surface builds up faster than in the bulk. When a critical concentration of vacancies is reached, melting is nucleated at the surface. Strański[7] has viewed melting as the dissolution of a solid in its own melt. He has observed that certain crystal surfaces facet and are wetted by their own melt, while other faces remain stable and are not wetted by the melt even at temperatures very near the melting point. These results led to a consideration of melting as a function of crystal surface. Melting in his context refers to the ability of a crystal face to support large concentrations of adsorbed atoms on its surface. The Strański model postulates that melting is initiated on high index faces; the low index faces being stable at all temperatures to the melting point. These melting models recognize the importance of surfaces in nucleating melting. Although they do not give a full description of the melting process and do not allow the prediction of the thermodynamic melting properties (such as volume change) or the statistical properties of melting (loss of long range order during the

phase transition) many of their assumptions are born out by experiments. There are several other melting models which describe either the thermodynamic or the statistical properties of melting without consideration of the importance of the crystal surface in nucleating and initiating melting. Perhaps the most notable and successful is that proposed by Lennard-Jones and Devonshire.[3] They adopted the Bragg-William model of one-dimensional order-disorder transition model in which the first order transition is generated with the help of the disorder parameter Q (which is equal to the number of atoms on ordered lattice sites relative to the total number of atoms). As the value of Q decreases (it varies between unity for the perfectly ordered lattice and one-half for the completely disordered solid), the energy to place an atom into a disordered site decreases--leading to the cooperative collapse of the ordered solid in a very narrow temperature range. Lennard-Jones and Devonshire assumed a 6-12 potential for the description of the crystal bonding and were successful in calculating many of the thermodynamic properties of argon melting [volume change upon fusion, entropy of fusion, etc.] However for other solids, such as carbon dioxide or metals which do not fit such a potential, their results differ greatly from the experimental values. Their theory is reasonable in predicting a melting transition with the appropriate physical characteristics. Applying this model using a pseudo-potential for metals might provide reasonable quantitative predictions for the melting properties. The addition of more realistic potentials may also make possible better descriptions of the kinetic barriers which cause substances to superheat and undercool or selectively melt at certain sites along certain crystallographic directions. Born[4] has considered the major difference between the solid and the liquid phase

is a lack of resistance of liquids to low frequency shearing stresses. Using the elastic continuum model he predicts that melting commences when the shear modulus of the crystal, c_{44}, vanishes ($c_{44} = 0$). Sound velocity measurements in different crystals however, did not bear out this prediction and the model was later retracted.[23] Kuhlmann-Wilsdorf has proposed a model in which the free energy of formation of a dislocation is taken as positive in solids and as negative for liquids. The melting temperature is postulated to be the temperature at which the free energy is zero. Thus, liquids are described as infinitely dislocated solids. The basic assumption of this model is supported by experimentally established properties of dislocations. Unfortunately, the calculated melting temperature is a function of the modulus of rigidity which is difficult to obtain accurately by experiments. A recent model proposed by Vladimirov[24] who viewed vacancies as the key defects rather than dislocations, also leads to reasonable predictions of some of the melting parameters.

We have found that slow freezing rates yielded dominantly the (111) surface orientation for lead and the $(01\bar{1}2)$ orientation [pseudo-cubic(100)] for bismuth crystallites. Conversely, rapid cooling rates produced the (100) orientation for lead and the (0001) [pseudo-cubic(111)] surface for bismuth. One might argue that, near equilibrium, lead which has to contract upon freezing should prefer to build its lattice from surfaces which show the densest packing of atoms [(111) face]. Bismuth, which expands upon freezing should prefer a more open surface [the $(01\bar{1}2)$ face] which still has low surface free energy. The result that growth conditions far from equilibrium (fast cooling rates) produce opposite surface orientations of the two solids should have to be taken into account in future theoretical studies of crystal growth kinetics.

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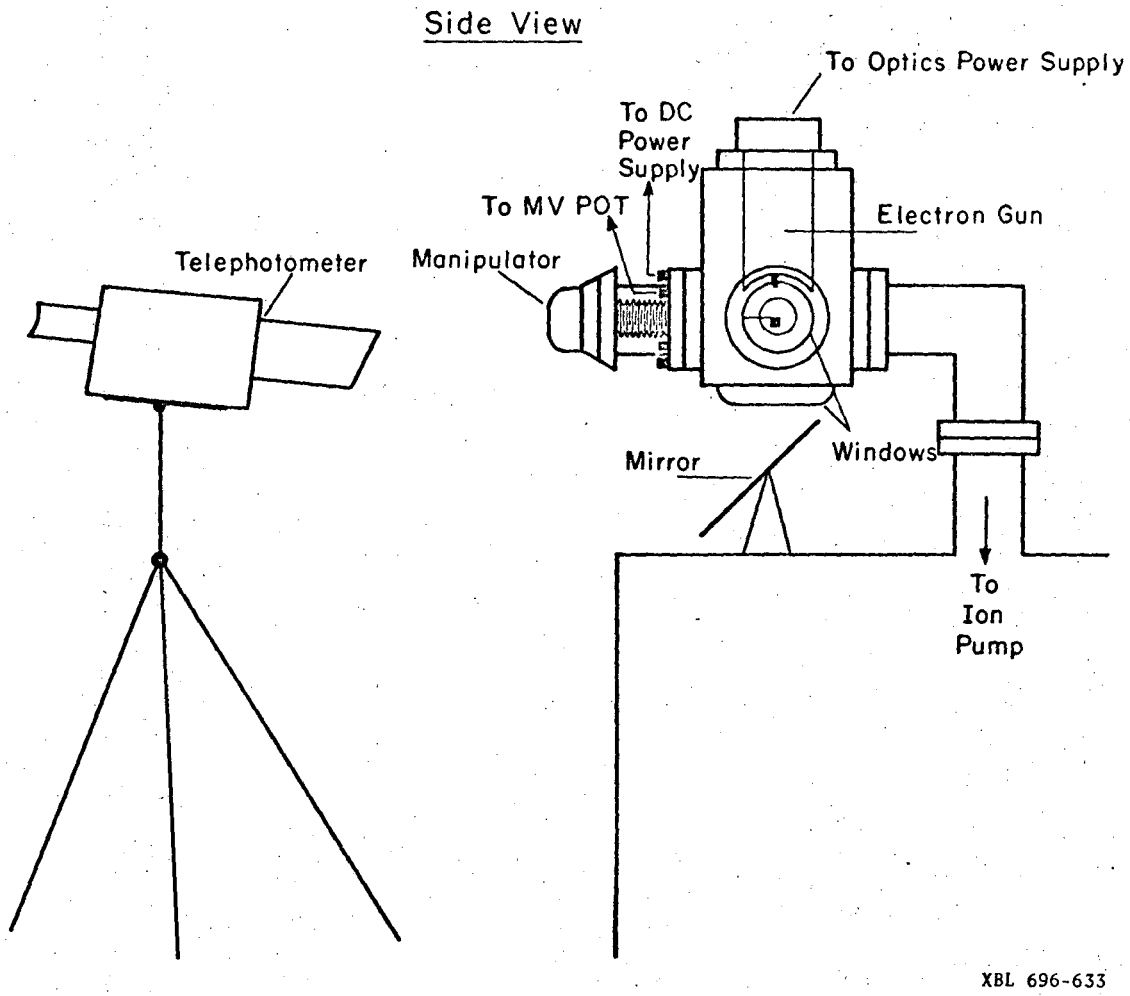


Figure 1a. Experimental arrangement for the melting experiments.

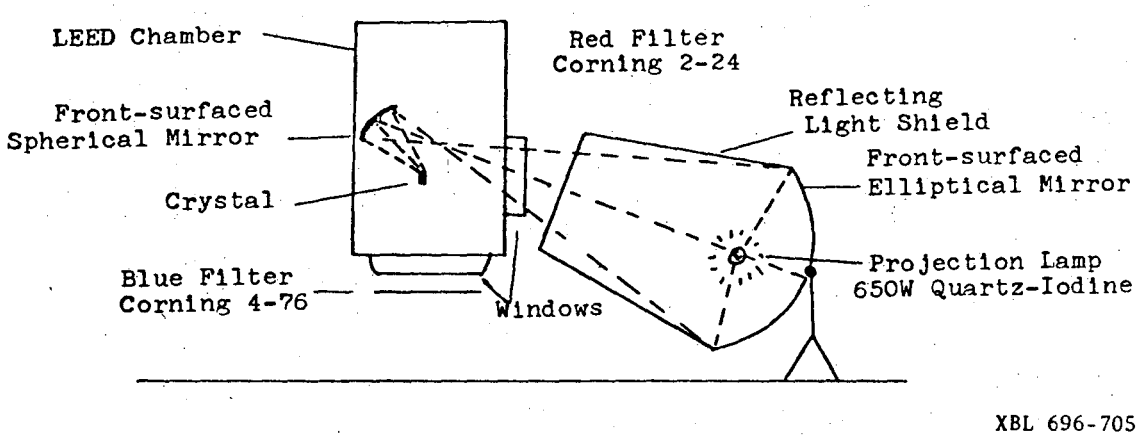
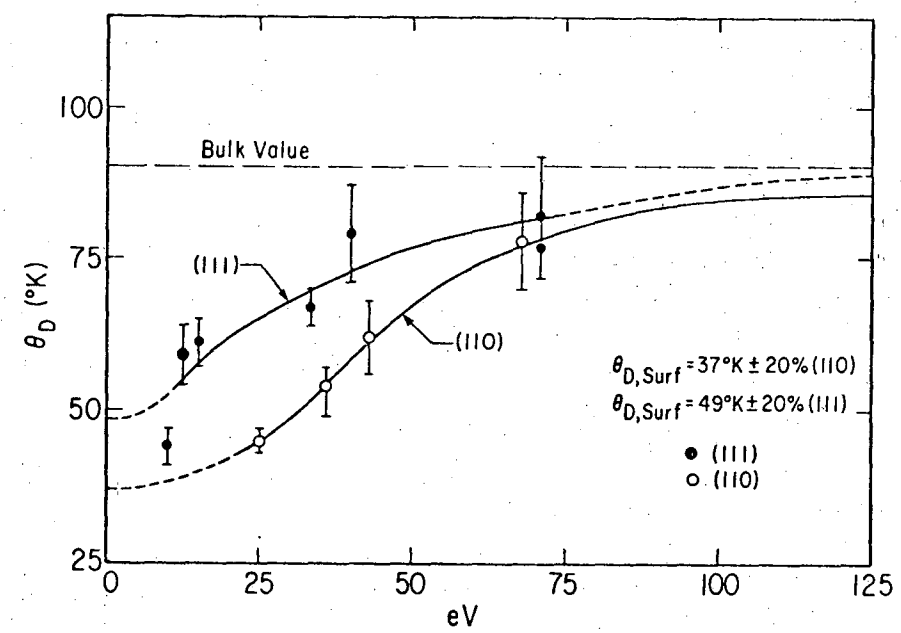
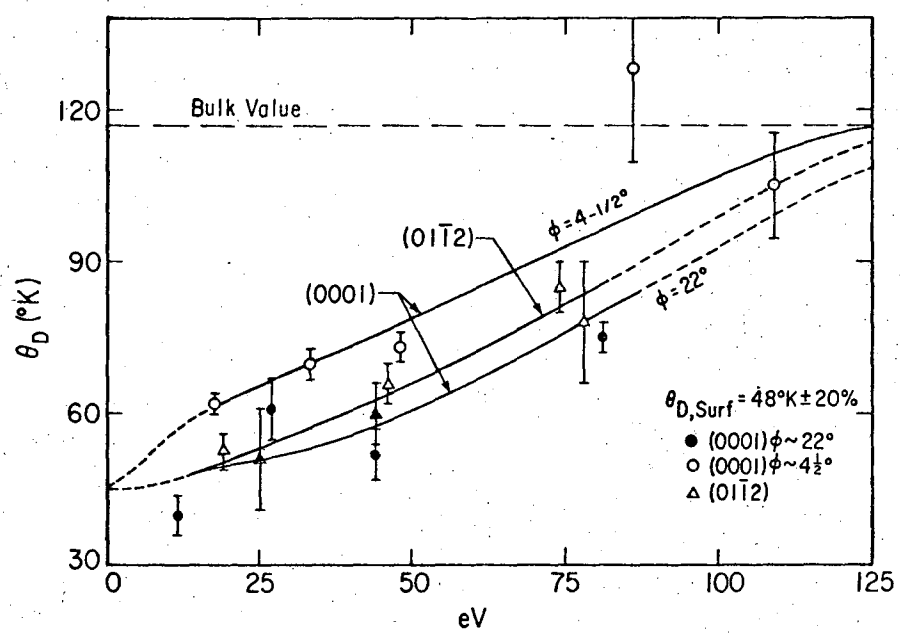


Figure 1b. Arrangement used for thermal image heating.

Figure 2a. Effective Debye temperature as a function of electron energy for the (110) and (111) faces of lead.





XBL 696-647

Figure 2b. Effective Debye temperature as a function of electron energy for the (0001) and (01$\bar{1}$2) surfaces of bismuth.

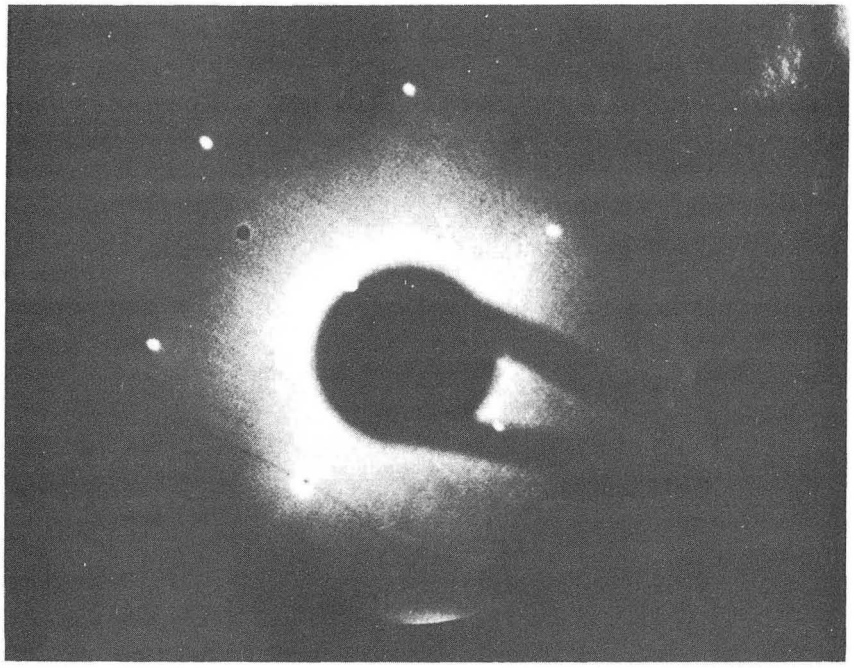


Figure 3a

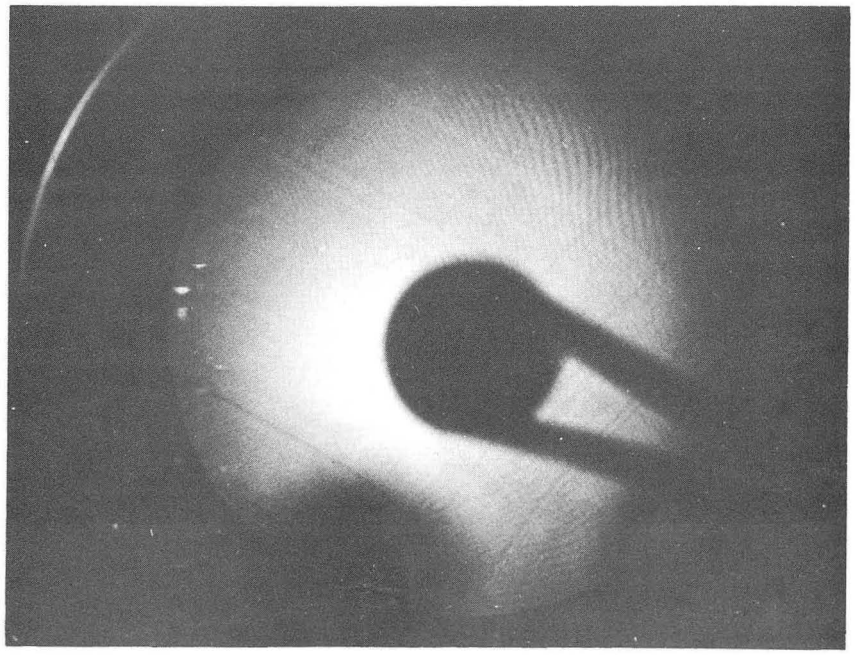


Figure 3b

XBB 6911-7608

Fig. 3a and 3b. Diffraction pattern of the Pb(111) surface at 61 eV a) below the bulk melting point (< 327°C) and of the molten surface b) above the bulk melting point (328°C).

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