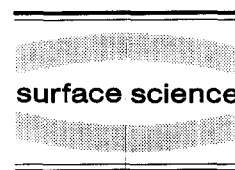




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On the (absence of) surface melting in biphenyl

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Abstract

The close packed (001) face of the anisotropic molecular crystal biphenyl has been studied using X-ray reflectivity upon approaching the melting point. No evidence for surface melting has been found, in contrast to the observations of Chernov and Yakovlev [Langmuir 3 (1987) 635] for the same crystal face against glass. We speculate that in the latter case the surface melting is not intrinsic but induced by the roughness of the glass.

Keywords: Biphenyl; Single crystal surfaces; Surface melting; X-ray scattering, diffraction, and reflection

1. Introduction

The experimental observation of a quasi-liquid layer wetting the solid–vapor interface below the bulk melting temperature T_m [1–12] has confirmed the old idea that the surface initiates the melting of a solid. So far experimental emphasis has been mainly on atomic systems like Pb(110) [2], Al(110) [3] and multilayers of Ar and Xe adsorbed on graphite [4]. In these cases of complete surface melting the thickness of the quasi-liquid layer diverges as the temperature approaches the bulk melting temperature T_m . In the case of incomplete or blocked surface melting, which has been observed in Ge(111) [5] and Pb(001) [6], the quasi-liquid layer remains finite at T_m . Anisotropic molecular crystals that have been inves-

tigated include ice [7–9], biphenyl [10,11] and caprolactam [12].

The growth of the quasi-liquid layer thickness is governed primarily by the range of the interactions in the system [1,13]. In systems governed by long-range Van der Waals interactions, such as Ar and Xe, the quasi-liquid layer thickness is found to show a power-law dependence on temperature. In the case of Pb and Al, where the short-range interactions dominate at low film thickness, there is a logarithmic dependence on temperature. For metallic crystals, however, the increasing importance of the long-range component upon approaching T_m can result in a cross-over from logarithmic to power-law growth, as observed on Pb(110).

Over the past years we have studied the surface melting of strongly anisotropic molecular crystals like caprolactam and biphenyl using X-ray reflectivity. In these crystals one might expect the geometric

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effects due to the anisotropy of the molecule to play an important role in the ordering of the quasi-liquid film and hence in the growth of the film thickness. Indeed, the surface melting of the caprolactam (100) face exhibits behavior previously not found in isotropic systems, such as layering transitions and a first-order pre-wetting transition [12]. In the case of biphenyl there has been an ellipsometry study indicating surface induced melting of this crystal against glass [10]. In this paper we report on an X-ray reflectivity study of the biphenyl (001) face against its vapor. No evidence for surface melting is found. We speculate that the surface melting reported against glass is not intrinsic but induced by the roughness of the glass.

2. Experimental

Biphenyl ($C_{12}H_{10}$) crystallizes below $T_m = 342.5$ K into a monoclinic $P2_1/a$ structure having lattice parameters $a = 8.12$ Å, $b = 5.63$ Å, $c = 9.51$ Å and $\beta = 95.1^\circ$ and two molecules per unit cell [14]. Single crystals were grown at a speed of 10^{-9} m/s from the melt of high purity zone-refined biphenyl. The resulting large cylindrical crystals were cut at liquid nitrogen temperature. The best samples had a typical size of about $20 \times 10 \times 7$ mm³, with the smallest dimension separating (001) faces. The crystal thus obtained was mounted into a snugly fitting recess in a copper block on the inner stage of a leak tight two stage oven and held in place by two steel tabs. To prevent excessive vaporization from the crystal the outer stage was loaded with biphenyl powder. The sample holder was then evacuated and filled with dry nitrogen. A smooth surface was obtained by the desorption of a number of surface layers. During the measurements both stages were resistively heated to the same temperature as measured by Pt100 resistors embedded in them.

The X-ray reflectivity experiments, which probe the density profile normal to the surface [15], were carried out on a triple axis spectrometer. Cu K α radiation ($k = 2\pi/\lambda = 4.075$ Å⁻¹) was obtained from an Enraf-Nonius GX21 rotating anode source operated at 8 kW. The scattering geometry has been described in detail elsewhere [16]. In brief, it employed a bent graphite monochromator which fo-

cused the beam in the out-of-plane direction onto the sample. Slits directly after the monochromator and directly before the sample defined the incident beam divergence, while slits before the detector defined the detector acceptance. A scan across the main beam gave a half width at half maximum (HWHM) of 0.1° . The entire sample was illuminated below $Q = 0.07$ Å⁻¹, where $Q = 2k\sin\theta$ is the wave vector transfer and θ the grazing angle of incidence. This is corrected for in the data shown. Specular scans were performed at various temperatures. Each point of the specular curve corresponds to an integrated specular intensity from a rocking curve at a fixed value of 2θ . In this way the sample mosaic (typically 0.3° FWHM) is integrated over, and the background, defined by the intensity at three times the peak width, is properly subtracted. With this procedure the value of the mosaicity limits the usable Q -range at the low end.

3. Results and discussion

Some typical reflectivity scans are shown in Fig. 1. All the scans showed a weak (001) Bragg peak at $Q = 0.33$ Å⁻¹ due to beam contamination with $\lambda/2$ from bremsstrahlung. The scans performed at a higher temperature indicate a rougher surface, and this roughness is reversible with temperature. Going

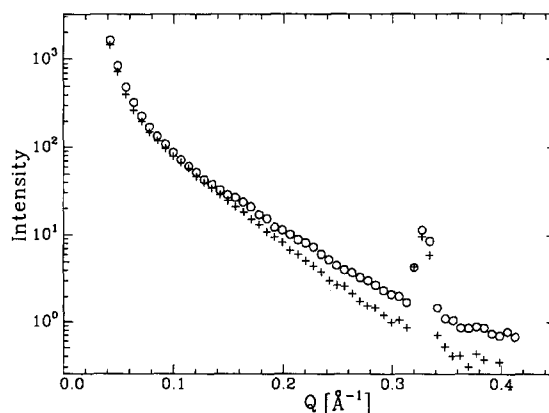


Fig. 1. Integrated specular reflected intensity of biphenyl (001) at 298.2 K (circles) and 336.2 K (crosses), respectively. The experimental results show an increased slope at the higher temperature, which is a signature of increased roughness, while the absence of oscillations implies that only one interface is present.

above 338 K the sample irreversibly roughened. For a single surface, the modulation of the specular intensity due to thermal roughening increases with Q as $\exp(-Q^2\sigma^2)$, where σ is the root mean square height variation of the surface, and increases with temperature T . The data qualitatively show the expected behavior with Q and T .

Surface melting necessitates in addition to the interface against vapor a quasi-liquid/solid interface. The X-ray photons reflected against each of the two interfaces will show interference. As a consequence the total reflected intensity will be modulated by oscillations, the period of which is determined by the thickness of the overlayer. Furthermore, the amplitude is proportional to the density difference between solid and quasi-liquid [17,12], which is for biphenyl estimated to be about 10% [14,18]. At the higher temperature presented in Fig. 1 Chernov and Yakovlev [10] report a molten overlayer of about 21 Å (for biphenyl against glass). Although this is not more than about twice the length of the molecule, from the optical changes reported in Ref. [10] and from the results for caprolactam [12] we could in the case of surface melting already expect a significant change in density. This would lead to clearly visible oscillations in the reflected intensity. The absence of such an effect in Fig. 1 indicates that the data can in principle be fitted by a one-interface model, and that most probably no surface melting occurs. Quantitatively the data do not fit very well to such a model due to a slight change of slope at $Q = 0.16 \text{ \AA}^{-1}$, which is attributed to the imperfect shape of the sample near the edges. Other samples measured at the NSLS in Brookhaven were of lower quality. Nevertheless these synchrotron results confirmed the absence of oscillations and thus provide no evidence for surface melting up to 2 K below T_m .

Surface melting occurs when [1]:

$$\Delta\gamma = \gamma_{sv} - (\gamma_{sl} + \gamma_{lv}) > 0, \quad (1)$$

where γ_{sv} , γ_{sl} , and γ_{lv} represent the surface energy (per unit area) of the solid–vapor, solid–liquid, and liquid–vapor interface, respectively. We must conclude that for the biphenyl (001) face this inequality is not satisfied. It should be noted that this face is known to be smooth in contact with the melt [19]. This is expected to result in strong layering interac-

tions, which would make any oscillations in the reflectivity easy to observe.

In their ellipsometric experiments [10] on biphenyl (001) against glass, Chernov and Yakovlev observed a quasi-liquid film at temperatures of about 15 K below the melting temperature. Since the interactions in this system are purely Van der Waals interactions, one might expect that surface melting would result in a quasi-liquid film whose thickness had a power law divergence on approaching the triple point. Instead, as they increased the temperature the film thickness initially showed a logarithmic growth followed within the last half of a degree below T_m by a cross-over to a power-law growth regime. Contrary to expectations for such an anisotropic crystal [11], they observed the same type of behavior on both the close packed (001) face and the relatively open (010) side face.

We propose two possible explanations for the difference between this work and the observations of Ref. [10]. For the experiment against glass in Eq. (1) γ_{sv} and γ_{lv} have to be replaced by γ_{sg} and γ_{lg} , where the latter indices refer to the solid–glass and liquid–glass interface, respectively. These changes might cause the inequality (1) to be satisfied so that surface melting can occur. However, this leaves the surprisingly similar behavior of both the (001) and the (010) face unexplained. For the close packed (001) face one might expect strong smectic-like layering to occur as the density modulation imposed by the crystal approximately matches the short range ordering in the liquid. In the case of the more open (010) side face, however, any density modulation imposed by the substrate would have a different periodicity that can hardly be expected to lead to strong layering. An alternative explanation of the difference between Ref. [10] and our results is suggested by the work of Beaglehole and Wilson [8]. They observed no surface melting for ice against smooth glass, but found that roughening of the glass can induce surface melting. In the latter case of extrinsic surface melting Eq. (1) changes into:

$$\Delta\gamma' = A(\gamma_{sg} - \gamma_{lg}) - \gamma_{sl} > 0, \quad (2)$$

where $A > 1$ is the ratio of the effective area associated with the glass interface to the area of the crystal–liquid interface. Now Eq. (2) can be satisfied even if this would not be the case for $A = 1$. Though we cannot unambiguously discriminate between the

two explanations, we tend to favor the latter one because it incorporates in a natural way the similar surface melting behavior against glass of the two very different faces of biphenyl.

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