

Surface premelting in Al(110) observed by core-level photoemission

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Surface premelting has been observed on Al(110) by recording Al 2*p* core-level photoemission at temperatures from $T=80$ K up to 1 K below the Al bulk melting point ($T_M=933.5$ K). By comparing spectra from Al(110) and Al(111) surfaces and from liquid aluminum the growth of a quasiliquid layer is established. The thickness of the layer is found to grow logarithmically with temperature, commencing at 150 K below the melting point, with a thickness of about 8 ML at 1 K below T_M . The degree of local structure and density of the quasiliquid layer are determined to be identical to those of liquid aluminum.

Surface premelting has received considerable attention in recent years. It is found that at temperatures near the melting point a quasiliquid layer may form on certain surfaces of the material under study.¹⁻³ More open surfaces have a higher tendency to exhibit surface premelting than close-packed ones. This phenomenon may serve to elucidate a number of experimental observations; for example, it provides a natural explanation for the fact that overheating of a solid does not occur, since the quasiliquid layer acts as a nucleation center for the melting process. The two most important properties which distinguish the quasiliquid layer from the crystalline bulk are density and long-range order. There have been a number of experiments which concentrate on surface order, using medium-energy ion scattering,² low-energy electron diffraction (LEED),⁴ and photoelectron diffraction;⁵ the density of the quasiliquid layer has been studied by means of x-ray reflection.⁶ Core-level photoemission is unique in its capability to address both properties simultaneously, since, as has previously been shown,⁷ core-level lines reflect local order and density through their Gaussian width and binding energy, respectively. Here we present a core-level photoemission study of surface premelting.

The photoemission spectra were obtained on the wiggler-undulator beam line at BESSY (Berliner Elektronen-Speicherring für Synchrotronstrahlung GmbH) using TGM 6 and TGM 5 monochromators at photon energies ranging from 80 to 110 eV. Photoelectrons were collected with a 50-mm hemispherical electron energy analyzer; the combined overall resolution of monochromator and analyzer was determined *in situ* using a retractable gas cell for photoemission from the Ar 3*p* level. It was found that after optimization the instrumental transmission function could be approximated to a high accuracy by a Gaussian. The best overall resolution was obtained on the TGM 6 monochromator yielding a Gaussian of 70-meV full width at half maximum (FWHM) at a photon energy of 82 eV. The samples were spark cut from a single-crystal rod to exhibit both (110) and (111) surfaces, and mechanically electropolished. They were mounted on a Mo sample holder encasing a ceramic insulated tantalum coil used for resistive heating. The experiments were performed at a base pressure of

3×10^{-11} mbar. The crystals were cleaned by cycles of neon sputtering at room temperature and elevated temperatures and annealing up to 900 K. Chemical and structural surface quality were verified by valence-band photoemission and LEED. All spectra were recorded in pairs from the Al(110) and (111) surfaces of the same sample at constant temperatures. Measurements and crystal heating were alternated with a frequency 30 Hz in order of guarantee that the photoemission data were not influenced by electric potentials or stray fields.⁸ The temperature was calibrated against the bulk melting point by melting the crystal at the end of an experiment; the temperature stability attained was on the order of 10 mK.

Al 2*p* spectra were measured with photon energies between 80 and 110 eV in order to cover the full range of surface sensitivity through photoelectron inelastic mean free paths of between 15 and 3 Å.⁹ A set of spectra of the well-resolved Al 2*p* doublet from Al(111) and Al(110), recorded at a photon energy of 98 eV at different temperatures, is shown in Fig. 1. The spectra from Al(111) consist of a single Al 2*p* line, represented by a broadened spin-orbit split pair of Doniach-Sunjic lines as shown for the 826-K spectrum, and of background intensity due to inelastic scattering and other processes^{7,10} not shown here. A small shift, and substantial broadening of the lines with increasing temperature, are observed. As presented in more detail elsewhere, these are due to thermal expansion, phononic coupling, and the temperature dependence of hole screening by Fermi-level electrons, with the broadening described by an increase in the Gaussian width of the line.⁷ It has also been shown that, for Al(111), surface and bulk emission occur at identical energies, making spectra of Al(111) representative of bulk emission from crystalline Al.⁷ For the bulk line all parameters except binding energy and Gaussian broadening are independent of sample temperature. In the evaluation of the spectra, a Lorentzian width [full width at half maximum (FWHM)] of 30 meV was used. The spin-orbit splitting was 411 meV, and a Doniach-Sunjic asymmetry parameter $\alpha=0.10$ was found. The determination of these parameters is discussed in detail elsewhere.⁷ The emission from Al(110), on the other hand, was found to contain a surface component, with a surface core-level (SCL) shift of (130 ± 10) meV as inferred from low-

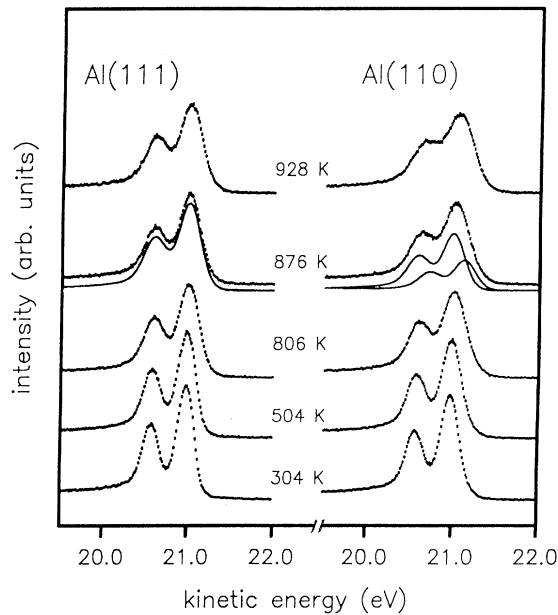


FIG. 1. Spectra of the Al $2p$ line recorded from Al(111) and Al(110) at different temperatures. Note the differences in line broadening at temperatures close to the melting point. The line-shape analysis used to evaluate the surface premelting process is shown for the 826-K spectra.

temperature data.

While the occurrence of a SCL accounts for the difference in the spectra from Al(110) and (111) in the low-temperature range, it is not sufficient to explain the large difference in the spectra close to the melting point. In order to arrive at an interpretation of the spectra at high temperatures, spectra recorded just below the melting point are compared with the spectrum of liquid Al just above the melting point in Fig. 2 [$T_M^{\text{bulk}}=933.5$ K

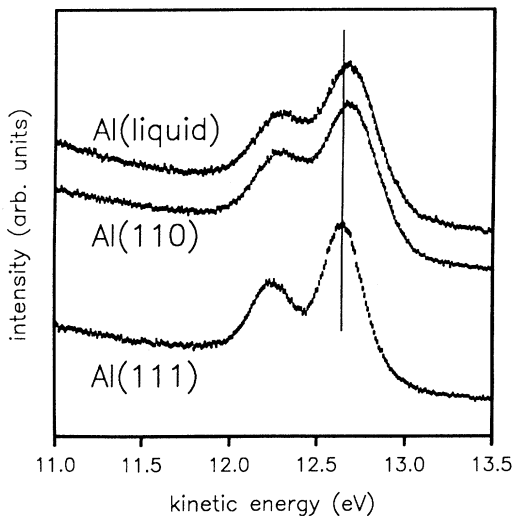


FIG. 2. Comparison of spectra from Al(111) and Al(110) about 2 K below the bulk melting point, with that from liquid Al recorded at 4 K above T_M .

(Ref. 11)]. It is clear that the spectra from Al(110) and liquid Al are identical, while both differ substantially from that of Al(111) in binding energy and broadening. We interpret this as evidence that the emission from Al(110) at this temperature (931 K) is dominated by electrons originating from a quasiliquid layer. Since binding energy and line broadening depend on density and the degree of local order, it follows that these properties of the top layer of the Al(110) surface correspond to liquid rather than bulk crystalline aluminum.

In order to interpret the data from different Al surfaces quantitatively, each spectrum was subjected to a line-shape analysis based on the following model. The Al $2p$ line from Al(110) is composed of two different contributions. One is due to bulk atoms, identical in width and energy to the emission from Al(111). The second component originates from a quasiliquid layer of thickness d at the surface; this component is broadened and shifted with respect to that of the bulk atoms (see the spectrum at 826 K in Fig. 1). A quantitative comparison of the spectra in Fig. 2 gives a shift in binding energy of 80 meV and an additional broadening of 190 meV for the line from liquid Al with respect to that from bulk crystalline Al at a temperature close to T_M . These values for shift and broadening were used to generate the second components from the respective bulk components at all temperatures.

At low substrate temperatures, a surface core-level shift (SCLS) of (130 ± 10) meV towards higher kinetic energies has also to be taken into account.^{8,12} A distinction between the SCLS component and emission from the quasiliquid layer is not feasible because of the close proximity of these lines and their relatively large intrinsic width. Thus we have not included an additional component for the SCLS in the line-shape analysis. Measures taken to ensure that this does not introduce errors in the results are discussed below.

This evaluation yields an intensity ratio of the emission from the quasiliquid layer and the bulk which, using the exponential decay law of the electron mean free path, enables us to measure the thickness of the layer at different temperatures; this is shown in Fig. 3 for different surface sensitivities as indicated by the symbols. The electron mean free paths used to convert the thickness into monolayers (the thickness of 1 ML is 1.43 Å) were chosen in order to reach the best agreement among results from different kinetic energies. The absolute value was determined to agree with independent experimental and theoretical results.⁹ The good agreement of the temperature dependence of the layer thickness resulting from different kinetic energies confirms our basic assumption of a separate layer at the surface. The mean free paths used (8.1 Å at 7-eV, 5.9 Å at 14-eV, 3.9 Å at 23-eV, and 3.0 Å at 35-eV kinetic energy) are in excellent agreement with those obtained from measuring the relative intensity of the surface-shifted component in Al(100), and with those calculated by Tung and Ritchie,⁹ except for the unexpectedly small value for $E_{\text{kin}}=7$ eV which may be due to large angle elastic scattering in the disordered layer. The apparent residual thickness of the quasiliquid layer at low temperatures in Fig. 3 is caused by the

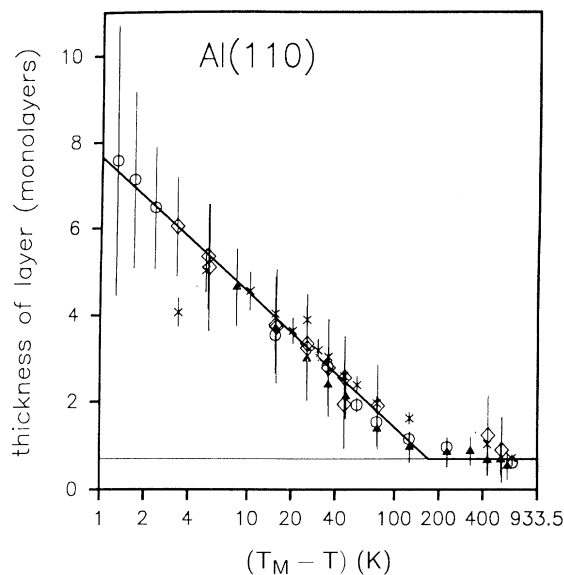


FIG. 3. Thickness of the quasiliquid layer on Al(110) as a function of temperature, derived from Al $2p$ line-shape analysis (see text). Symbols refer to spectra recorded with different photon energies; average kinetic energy is 35 eV for open circles, 23 eV for crosses, 14 eV for triangles, and 7 eV for diamonds.

neglect of the surface core-level-shifted component in the evaluation; it represents emission from the surface layer. Since the bulk line broadens with temperature, the magnitude of the contribution from the SCL emission to the quasiliquid component might change, giving rise to a spurious temperature dependence. In order to avoid this possible error, all pairs of spectra were numerically broadened in order to achieve an equal and temperature-independent Gaussian width of 300 meV of the Al(111) line before determining the relative intensity of the quasiliquid layer emission. The results in Fig. 3 are based on this procedure. The increase in the thickness of the layer is found to depend linearly on the logarithm of $(T_M - T)$. The onset of the formation of the quasiliquid layer occurs at (150 ± 20) K below T_M . At 1 K below T_M , the quasi-molten layer has a thickness of (8 ± 3) ML close to the limit of our thickness determination because of the high surface sensitivity of the photoemission experiment; this is the reason for the increasingly large error bars on the

data points as T_M is approached.

Surface premelting in Al(110) has been investigated with ion scattering by van der Gon *et al.*,¹³ and with x-ray diffraction by Dosch *et al.*¹⁴ van der Gon *et al.* found the onset of a quasiliquid layer at 117 K below T_M for Al(110), with a thickness of 5.4 ML at 1 K below T_M . No quasiliquid layer was found in Al(111). Dosch *et al.* measured the temperature dependence of the (002) beam up to 80 K below the bulk melting point, and found that in the temperature regime above 770 K, i.e., at about 160 K below T_M , the intensity and profile could be best described by surface layers which do not exhibit Bragg scattering, i.e., which are completely disordered, and the thickness of which increased with temperature. There is good agreement about the onset of surface premelting between our experimental data and the results of van der Gon *et al.* and Dosch *et al.* within the error margins of the experiments.

Ion-scattering and diffraction methods have played a key role in the investigation of surface melting. However, both methods are primarily sensitive to disordering effects, i.e., the displacement of surface atoms from their lattice sites, which leads to an attenuation of diffracted intensity, or an increase of atoms visible to the ion beam. As demonstrated above, core-level photoemission is directly sensitive to the change in density in the surface region as the quasiliquid layer forms. Angular profiles of x-ray reflectivity are sensitive to the density of the surface layer, and have been utilized by Pluis *et al.*⁶ for the measurement of layer density; however, this method is less surface sensitive, such that in the case of Pb(110) the density decrease from the solid to the liquid could only be measured within a few degrees below T_M . The present photoemission results offer an additional contribution to the study of surface premelting processes not provided by other methods so far, since they are simultaneously sensitive to the order in the surface, are reflected in the width of the photoemission line, independent of surface orientation, and to the density of the quasiliquid layer, through the line energy.

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