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Ch. Grütter[1], P. Reinert[1], U. Dürig[2], and J. H. Bilgram[1]

[1]Laboratorium für Festkörperphysik
Eidgenössische Technische Hochschule
8093 Zürich
Switzerland

[2]IBM Research Division
Zurich Research Laboratory
8803 Rüschlikon
Switzerland

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Ch. Grütter[1], P. Reinert[1], U. Dürig[2], and J. H. Bilgram[1]

[1]*Laboratorium für Festkörperphysik, Eidgenössische Technische Hochschule, 8093 Zürich, Switzerland*

[2]*IBM Research Division, Zurich Research Laboratory, 8803 Rüschlikon, Switzerland*

Abstract

The surface structure and the melting behavior of Ga(112) and Ga(100) surfaces have been studied by means of STM, LEED, ellipsometry, and laser heating. A 1×4 reconstruction of the missing-row type has been discovered at the Ga(112) surface. It stabilizes this surface in such a way, that the surface can be superheated by more than 0.1 K. The Ga(100) surface does not reconstruct. A layer of an anisotropic quasiliquid is found, which has a thickness of about 4 nm close to the melting temperature.

Can crystals be superheated with respect to their bulk melt? In every day life superheated crystals have never been observed, therefore it has been thought for a long time that crystals cannot be superheated. About 15 years ago it has been found that crystals can be superheated if the surface of a crystal can be prevented from melting. Then the question has changed to: Why is there no nucleation barrier to form a liquid at most crystal surfaces? It has been found as a rule that crystal surfaces with low packing densities have higher free energies than surfaces with high packing densities. Therefore surfaces with low packing densities are expected to reduce their surface free energies by a surface reconstruction or by surface melting. The long-range order at crystal surfaces disappears at temperatures below the equilibrium melting temperature T_m and a "quasiliquid" layer is formed during surface melting [1]. Ice is the best known substance which forms a quasiliquid layer [2]. The equilibrium thickness ℓ^* of a thin quasiliquid layer is given by [3]

$$\ell^*(T) = \frac{\xi}{2} \ln \left[\frac{2\,\Delta\gamma\, T_\mathrm{m}}{L_\mathrm{m}\,\xi(T_\mathrm{m} - T)} \right] \quad , \tag{1}$$

where L_m and ξ are the latent heat of melting per unit volume and the density–density correlation length in the quasiliquid. $\Delta\gamma$ is the free energy gained upon surface melting.

To obtain information on the behavior of crystal surfaces at conditions close to the melting transition we perform combined experimental studies of optical and microscopic properties of surfaces of α-Ga single crystals at temperatures up to 0.1 K above T_m. Ellipsometry is used to determine optical properties, whereas low energy electron diffraction (LEED) and scanning tunneling microscopy (STM) are used to determine structural and microscopic properties. Superheating of crystal surfaces is studied by laser heating.

Ga is an ideal substance for an investigation close to T_m [T_m(Ga) $= 29.774\,^\circ$C]. Because of the low vapor pressure, sublimation can be neglected in ultra high vacuum (UHV). Due to large anisotropies the solid can be easily distinguished from a melt. The crystal structure of α-Ga is face-centered orthorhombic with eight atoms per unit cell. Each atom has only one nearest neighbor. Structural details are given in [4]. Four low-index facets are formed at Ga crystals during growth from the melt: Ga(112), Ga(100), Ga(111) and Ga(010); in the sequence of increasing packing density. Surface properties of Ga(010) at low temperatures ($T < T_\mathrm{m}$) have been studied recently [4–7].

In this Letter properties of Ga(112) and Ga(100) at temperatures close to T_m are presented. We use surfaces of Ga-single crystals grown under UHV conditions. The base pressure in the measuring chamber is 10^{-10} mbar. Prior to measurements all crystals have been cleaned by argon sputtering and analyzed by Auger electron spectroscopy. T_m is approached within 0.01 K in the optical analysis chamber. For details of the experimental setup see [8].

The Ga(112) surface lowers its free energy by a surface reconstruction. This has been detected by means of three experimental techniques.

(i) A first indication for surface reconstruction has been found from ellipsometric measurements. The index of refraction n and the coefficient of optical absorption k are anisotropic, and the orientations of the extrema of n and k do not coincide as it is expected for an orthorhombic bulk structure.

(ii) LEED patterns show a superstructure corresponding to a (1×4) reconstruction perpendicular to the $[1\bar{1}0]$ direction.

(iii) Details of this reconstruction have been obtained from STM images. Fig. 1 was taken at $11.5\,^\circ$C and shows a representative area of 132 Å $\times$ 132 Å.

From the STM images one can conclude that the reconstruction is of the "missing-row" type. The surface structure does not change if the crystal is heated up to $29.5\,^\circ$C. Surprisingly STM studies could be performed without difficulties up to temperatures close to T_m, which is a strong indication for the stability of this surface. The period of the reconstruction perpendicular to the $[1\bar{1}0]$ direction is (37 ± 1) Å, corresponding to four times the width of the unit cell perpendicular to the $[1\bar{1}0]$ direction (0.9005 nm). This observation is in quantitative agreement with the LEED pattern. To obtain a microscopic picture of the reconstruction we start from the truncated bulk as it is shown in Fig. 2. By removing two top rows per period as indicated by arrows in Figs. 2(a) and (b), we arrive at a model of the "missing-row" reconstruction which is in good qualitative agreement with our STM data. In the top view, Fig. 2c, the marked rows are removed. The observed corrugation is almost in quantitative agreement with the suggested missing-row model. Two features observed in the STM topographies are in difference to the model. The double rows do not have the same height and the absolute value of the corrugation of the reconstruction is in the topography not as pronounced as in the model. Both features indicate that the missing-row reconstruction is accompanied by a relaxation, a phenomenon generally observed at metal surfaces.

Ellipsometry experiments confirm the stability of the Ga(112) surface. No changes of the ellipsometric data were observed up to a temperature $T \approx T_{\mathrm{m}} + 0.1$ K. The surface is stable at least up to 0.1 K above T_{m}. This stability was further confirmed by a simple experiment: The crystal was thermostated at T_{m}. Then the measuring area of the ellipsometer was heated additionally by a focused Ar-laser beam of 100 mW for several minutes. Melting started not at the illuminated area but at the edges of the crystal and propagated inwards to the center of the surface where measurements were performed.

The behavior found for the Ga(100) surface is markedly different. The LEED pattern of the Ga(100) surface corresponds to the calculated spots obtained from the truncated bulk. This indicates that the surface is not reconstructed and the surface free energy might be reduced by surface melting. In Fig. 3 ellipsometric measurements of the optical constants are plotted in function of the direction on the crystal surface.

Studies of the temperature dependence of the optical properties were performed in the temperature range $27.4\,^\circ\mathrm{C} < T < (T_{\mathrm{m}} - 0.04\,^\circ\mathrm{C})$ along three directions labeled in Fig. 3 by **A**, **B** and **C**. **A** is the direction of n_{max}, **C** the direction of n_{min} and **B** one direction of the Ga-dimer axes (see inset in Fig. 3). In the measurements along the direction **A** continuous changes in the optical properties have been observed, when the temperature increased. Subsequent cooling down showed that the measurements were fully reversible within the precision of our measurements. No hysteresis effects were detected. From this observation we conclude (i) the surface undergoes premelting, (ii) premelting is not a first-order transition, and (iii) the crystal is always in thermal equilibrium.

In the following we interpret the changes in the ellipsometric data in terms of the formation of a quasiliquid layer at the Ga(100) surface. For the determination of the optical constants, and the thickness of the quasiliquid layer, we use the method developed by Urban and Comfort [9]. We assume that the optical constants of the layer do not change with increasing layer thickness.

From our data analysis the following properties of the surface layer emerge:

(1) In the direction **A** we obtain for the layer $n = 5.79 \pm 0.07$ and $k = -4.39 \pm 0.08$. The corresponding value of the substrate is 0.22 ± 0.05 larger for n and 0.01 ± 0.04 larger for k. The optical properties of the substrate, the Ga crystal, have been determined at temperatures well below T_{m} (about at $26\,^\circ\mathrm{C}$). Thus, n of the layer is in between the solid and the liquid, but much closer to the solid; k remains at the value of the solid. The optical properties of the liquid have been determined in a separate experiment: $n_{\mathrm{liquid}} = 1.57 \pm 0.04$, $k_{\mathrm{liquid}} = -7.29 \pm 0.11$.

(2) Along the direction **B** n is closer to the value of the bulk, whereas k remains unchanged at the value of the bulk, within the precision of our measurements. No temperature dependence of n nor of k has been found along direction **C** up to $T_{\mathrm{m}} - 0.04\,^\circ\mathrm{C}$. We conclude that the layer

is anisotropic.

(3) n, k and the thickness ℓ^* of the quasiliquid layer can be deduced from the ellipsometric data. ℓ^* is plotted in Fig. 4 vs. temperature. The thickness grows logarithmically and at the temperature $T_\mathrm{m}-0.04\,^\circ$C, ℓ^* is approximately 4 nm, which corresponds to about 18 monolayers. Unlike n and k, ℓ^* does not depend on the direction at the crystal surface. This experimental result confirms our simple model of the quasiliquid layer.

4) The correlation length ξ within the quasiliquid can be determined using Eq. (1). From the logarithmic growth law observed in the experiments $\xi = (3.9 \pm 1.2)$ nm is found. This value is significantly larger than the typical correlation length in bulk liquid Ga, which was found in x-ray scattering experiments to be $\xi_\mathrm{l} = (0.58 \pm 0.04)$ nm [10]. This indicates that there is still some order remaining in the quasiliquid layer.

For a study of the surface at $T > T_\mathrm{m}$, we have performed again a laser heating experiment. Now a HeNe laser ($P = 15$ mW) is used to illuminate a surface which has been brought in thermal equilibrium at T_m. After about 20 s the surface started to melt at the illuminated spot. The boundaries of this molten region agreed perfectly with the directions of the edges of the Ga(100) facet, which are the [011] and the $[1\bar{1}0]$ directions. These boundaries correspond to the intersection of the (100) with the (111) facet. No roughening seems to occur at these boundaries at the melting point. As T_m isotherms at the surface are ellipses, we conclude from the occurrence of the straight boundaries of the liquid pool that the surface is locally superheated. This is confirmed by a second observation: At the melting point the crystal started to melt from the edges of the facets but not in the region of the premelted layer. From this we conclude that the thickness of the layer does not diverge and does not change its properties to the ones of bulk melt in a continuous process. Surface melting on this surface is blocked. This conclusion is in agreement with calculations of the Hamaker constants of surfaces of Ga which predict blocked melting [11].

We did not include in our discussion surface roughening. If the observed changes in the ellipsometric data would be caused by roughening, they would be independent of the direction on a surface, and roughening could be identified from the absolute changes in the ellipsometric data [12].

The truncated bulk structures of the two surfaces of Ga studied in the experiments reported in this Letter have both low packing densities and therefore both might become unstable at T_m. We have selected these two surfaces because they demonstrate how such surfaces can develop at in different ways, both leading to a reduction of surface free energy. The Ga(112) surface shows a 1×4 reconstruction, which turns out to be very stable and can be superheated by more than $0.1\,^\circ$C. The missing-row reconstruction is similar to reconstructions found at the (100) surfaces of gold and platinum [13]. At the Ga-(100) surface continuous and reversible changes of the optical properties are observed if the temperature approaches T_m. The largest changes in n are observed in the direction of the [010]-axis. This can be compared with experiments on and simulations of fcc(110) surfaces of other metals, where largest effects of premelting and strongest disordering was detected along the direction, where distances between atoms are smallest [14]. In the case of the Ga(100) surface, shortest distances, i.e. the distances between two nearest neighbors, are lying (averaged over the two possible tilting directions of the Ga dimers) along the b-axis. Therefore strongest disordering is expected along the [010] direction. This is in agreement with our observations. Thus we conclude that at the Ga(100) surface a layer of an anisotropic quasiliquid is formed below T_m.

ACKNOWLEDGMENTS

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[1] J. G. Dash, Contemp. Phys. **30**, 89 (1989).
[2] H. Dosch, A. Lied, and J. H. Bilgram, Surf. Sci. **366**, 43 (1996).
[3] B. Pluis, D. Frenkel, and J.F. van der Veen, Surf. Sci. **239**, 282 (1990).
[4] D. A. Walko, I. K. Robinson, Ch. Grütter, and J. H. Bilgram, Phys. Rev. Lett. **81**, 626 (1998).
[5] O. Züger and U. Dürig, Phys. Rev. B **46**, 7319 (1992)
[6] M. Bernasconi, G. L. Chiarotti, and E. Tosatti, Phys. Rev. Lett. **70**, 3295 (1995).
[7] Ph. Hofmann, Y. Q. Cai, Ch. Grütter, and J. H. Bilgram, Phys. Rev. Lett. **81**, 1670 (1998).
[8] R. Trittibach, Ch. Grütter and J. H. Bilgram, Phys. Rev. B **50**, 2529 (1994).
[9] J. C. Comfort and F. K. Urban III, Thin Solid Films **270**, 78 (1995); F. K. Urban III and J. C. Comfort, J. Vac. Sci. Technol. A **14**, 2331 (1996).
[10] M. Regan, E. Kawamoto, S. Lee, and P. Pershan, Phys. Rev. Lett. **75**, 2498 (1995).
[11] A. Dal Corso and E. Tosatti, Phys. Rev. B **47**, 9742 (1993).
[12] D. W. Berreman, J. Opt. Soc. Am. **60**, 499 (1970); S. J. Fang, W. Chen, T. Yamanaka, and C. R. Helms, Appl. Phys. Lett. **68**, 2837 (1996).
[13] J. Villain, J. L. Rouvière, and I. Vilfan, in *Phase Transitions in Surface Films 2*, edited by H. Taub *et al.* (Plenum Press, New York, 1991).
[14] A. Landa, P. Wynblatt, H. Häkkinen, R. N. Barnett, and U. Landmann, Phys. Rev. B **51**, 10972 (1995); K. C. Prince, U. Breuer, and H. P. Bonzel, Phys. Rev. Lett. **60**, 1146 (1988); H. Löwen and T. Beier, Phys. Rev. B **41**, 4435 (1990).

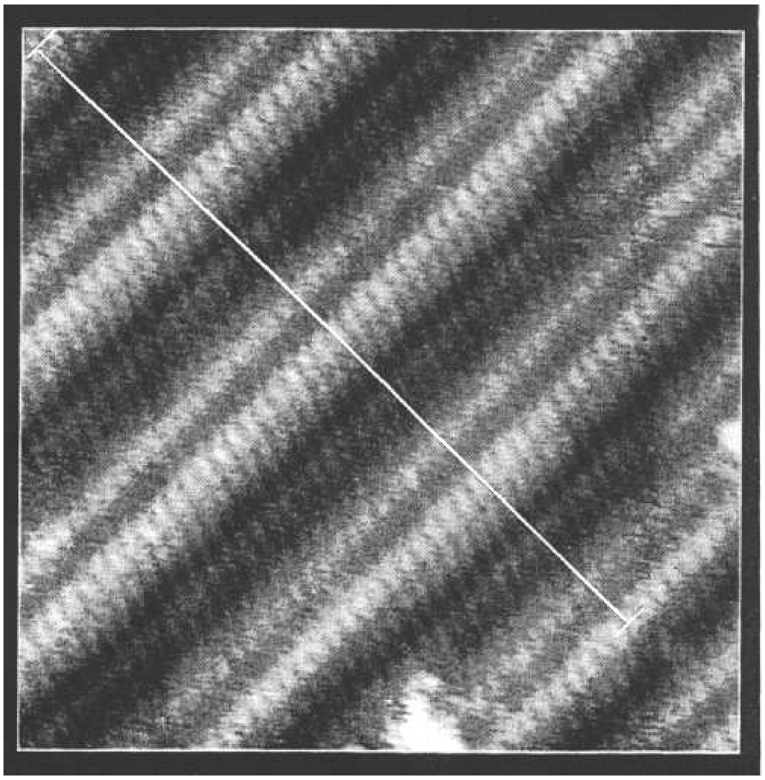

FIG. 1. STM scan of the surface with a size of 132 Å $\times$ 132 Å. The reconstruction consists of double rows. Two double rows are separated by two deeper-lying rows. A height profile along the cross-section line is depicted in Fig. 2(b).

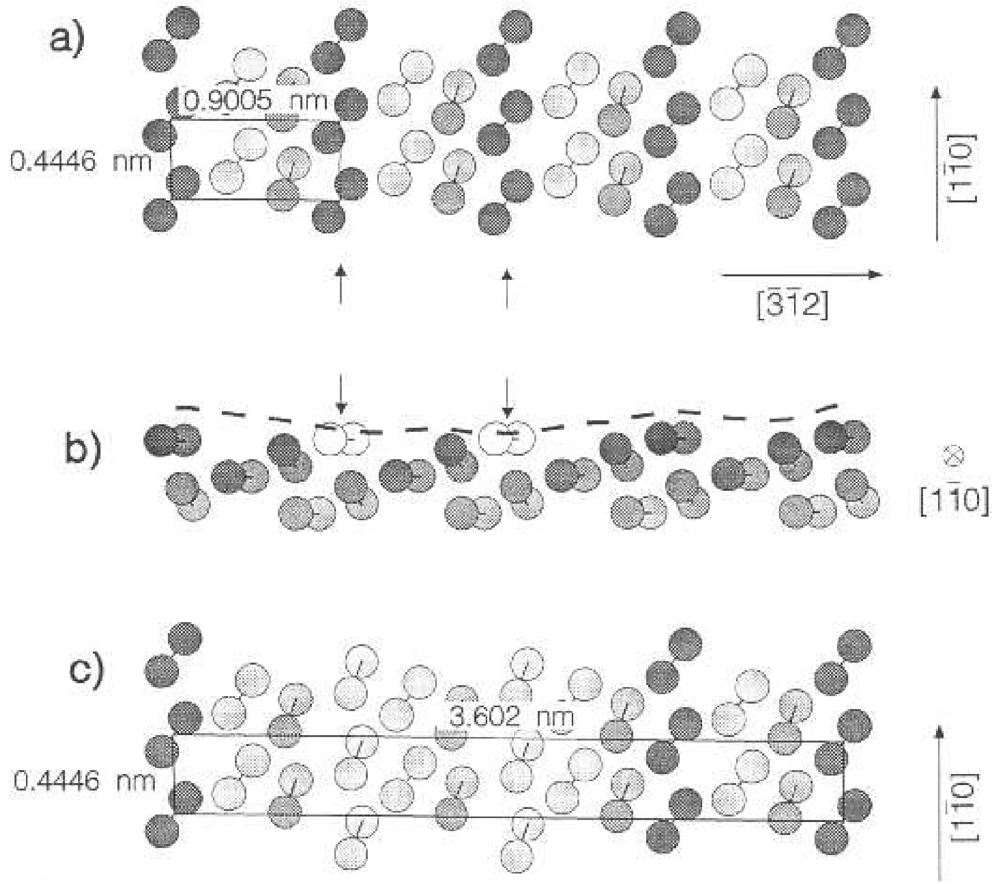

FIG. 2. (a) Top view on the Ga(112) surface obtained from the truncated bulk. (b) Side view along the [1$\bar{1}$0] direction. The dashed line represents a height profile measured by means of STM along the diagonal line in Fig. 1. A model of the reconstructed surface is obtained by removing two rows from the unreconstructed surface [indicated in (a) and (b) by arrows]. (c) Top view on the reconstructed surface, i.e. two rows per period are removed. Dark atoms represent a higher level than white atoms. The surface unit cells of the truncated bulk and the reconstructed surface are indicated by squares (a) and (c).

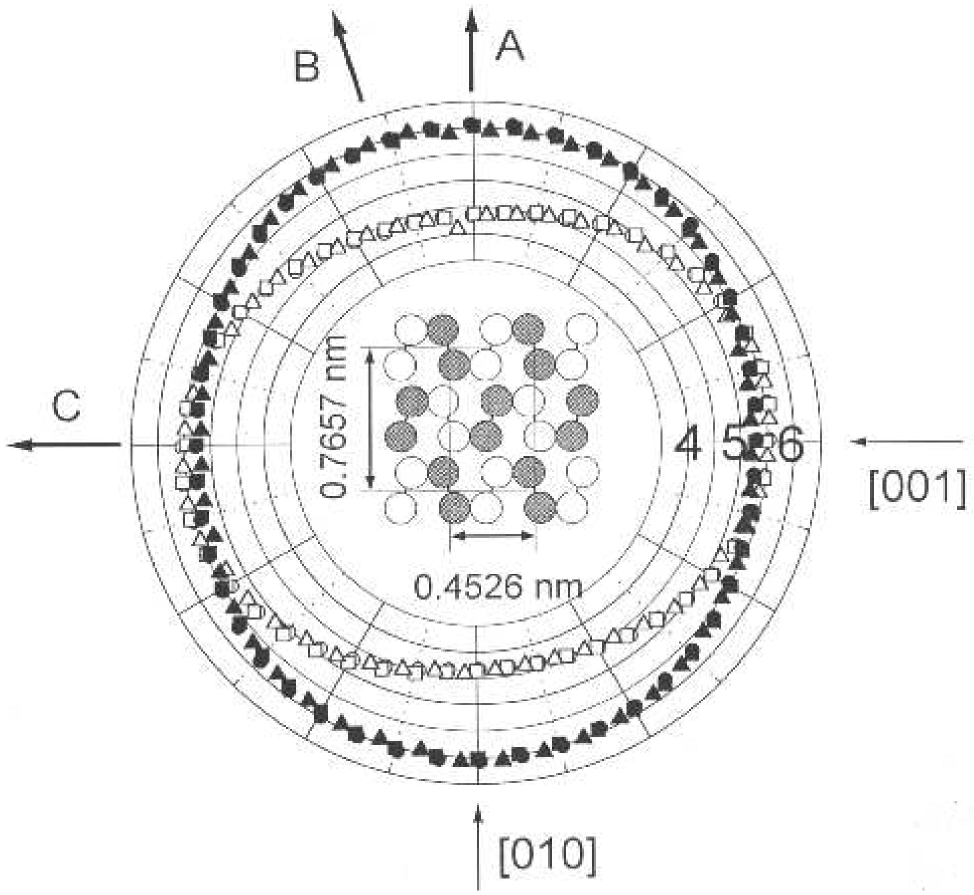

FIG. 3. Optical constants n (solid symbols) and $-k$ (open symbols) at the Ga(100) surface as deduced from ellipsometric measurements are plotted as a function of crystal direction on the surface. Measurements have been performed well below T_m at about 26 °C. To show the good reproducibility, measurements on three different crystal surfaces marked by circles, squares and triangles are plotted. Error bars are smaller than the size of the symbols. The directions of the principal axes lying in the Ga(100) surface are indicated. Measured values of the data range from 3.5 to 6.5. The inset in the center of the plot shows a top view of the atomic structure, as deduced from the truncated bulk, where the dark atoms are lying in the top layer and open atoms in the second layer. The square indicates the surface unit cell. Temperature dependence of n and k has been measured along the directions labeled with **A**, **B**, and **C**.

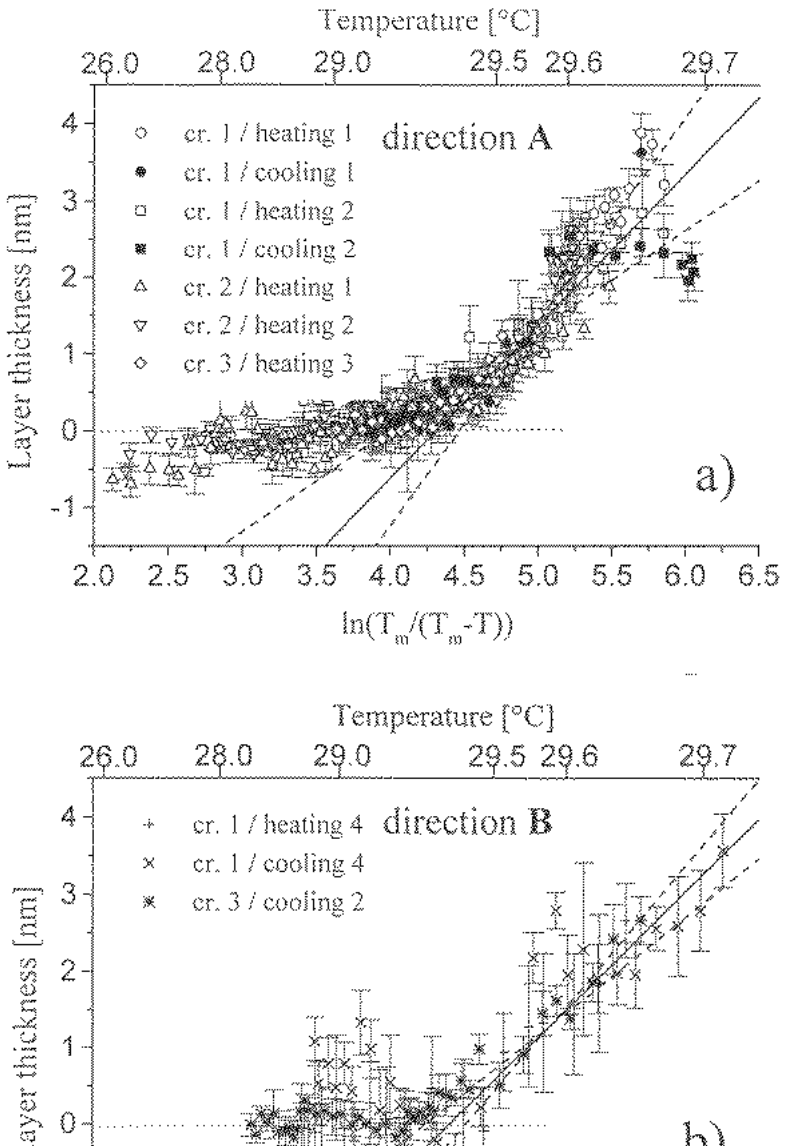

FIG. 4. Layer thickness ℓ^* vs. $\ln(T_\mathrm{m}/(T_\mathrm{m}-T))$. (a) For measurements in direction $n_{\max}$ (**A**). Open symbols represent measurements heating up to T_m and solid symbols cooling down. Measurements were performed on three different crystals (cr. 1 to 3). The solid line is a fit to all data in the region where a quasiliquid layer exists, with dashed lines indicating the errors. The dotted line marks zero layer thickness. (b) Measurements along the direction of the molecule axes (**B**).