

Near-Surface X-Ray Critical Scattering from a NH_4Br ($\bar{1}\bar{1}0$) Surface

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We present the first observations of near-surface critical phenomena of a phase transition in a molecular solid showing both an order-disorder and a strong displacive component. The surface x-ray scattering experiments were performed on an NH_4Br single crystal ($T_c = 235$ K). For the order parameter they show a crossover from a power law with the bulk critical exponent $\beta = 0.3 \pm 0.05$ to a surface behavior with exponent $\beta_1 = 0.8 \pm 0.1$. From the diffuse intensity we have determined the critical exponents $\eta_{\parallel} = 1.3 \pm 0.15$, $\nu = 0.5 \pm 0.15$ and the correlation length $\xi_0^+ = 4 \pm 0.5$ Å.

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In the past few years there has been great interest in the critical behavior of phase transitions in the near-surface region. The broken translational symmetry at the surface leads to a modified criticality [1, 2]. There are three possible types of phase transitions induced by the surface: (i) the “ordinary” transition with the same transition temperatures in the bulk and at the surface, (ii) the “extraordinary” case where the ordering of the surface occurs at a higher temperature (“surface transition”) than in the bulk, and (iii) the “special” transition representing a multicritical point separating the types mentioned above. For each of these transitions new surface-related critical exponents occur. However, the length scale of the critical fluctuations remains to be the bulk correlation length ξ . In the case of the ordinary transition there is only one additional exponent, while the other surface exponents can be expressed as combinations of the new one and the bulk values via scaling relations. In theoretical studies many detailed predictions have been made also introducing new methods for precision determinations of critical parameters [1, 3]. For experimental investigations of critical phenomena at surfaces Dietrich and Wagner proposed x-ray and neutron diffraction [4]. A detailed review of both theoretical and experimental aspects concerning the surface scattering is given by Dosch [5].

So far the experiments were concentrated on magnetic systems and order-disorder transitions in alloys. The first observations of the temperature behavior of the surface order parameter have been made on the magnetization of Ni surfaces by Celotta *et al.* [6] and Alvarado *et al.* [7]. Especially the latter yielded the predicted power law with the critical exponent $\beta_1 = 0.825 \pm 0.04$. Surface x-ray scattering investigations on the order-disorder transitions in Cu_3Au and, more related to second order phase transitions, Fe_3Al were carried out by Dosch and co-workers [8, 9] and verified the theoretical predictions even better. In particular, all surface exponents could be determined independently and the scaling relations could be tested

[9]. Furthermore, Toennies and Vollmer [10] performed a helium atom scattering study on a KMnF_3 surface. For this structural (distortive) phase transition their experiment yielded $\beta_1 = 0.63 \pm 0.03$. This exponent is too small for an ordinary transition in the Heisenberg model but in reasonable agreement with the (also too small) experimental bulk value.

In this work we report the first study of near-surface critical phenomena of a phase transition in a molecular solid. NH_4Br shows at $T_c = 235$ K a nearly continuous order-disorder transition with a strong displacive component. In many respects this is an ideal example for studying the surface-induced critical exponents as predicted for continuous phase transitions.

When cooling bulk NH_4Br from the orientationally disordered room temperature phase (cubic, space group $Pm\bar{3}m$), the orientation of the ammonium tetrahedra becomes antiferro-ordered in the ab plane and ferro-ordered along the c axis (tetragonal, space group $P4/nmm$). In addition to this order-disorder aspect there is a small displacement of the bromine ions [11, 12] which is part of the ordering mode and hence the order parameter. An appropriate description of the critical fluctuations of this pseudospin system is given by the 3D Ising model. However, this transition has a small first order component. In bulk experiments the temperature dependence of the order parameter was observed with an exponent of $\beta = 0.25$ [13]. This is less than the Ising value $\beta = 0.32$ and probably due to the first order component. In our diffraction experiments we observe the displacive transition via the coupling of the x rays to the bromine displacements, but not to the orientational order.

For x rays the index of refraction is slightly less than unity and so the phenomenon of total external reflection occurs. Below the critical angle α_c the electromagnetic wave is exponentially damped in the z direction and propagates along the surface. For a larger angle of incidence α_i the x rays penetrate deeper into the crystal. The scattering depth Λ is given by

$$\Lambda = |\text{Im}(Q_z)|^{-1}. \quad (1)$$

Here Q_z denotes the momentum transfer parallel to the surface normal inside the crystal. Within the distorted wave Born approximation [5], the scattering law $S(Q_z, Q_{\parallel})$ is modified by the Fresnel transmission functions T_i and T_f of the incident and outgoing fields, respectively, and therefore the scattered intensity is given by

$$I = |T_i|^2 S(Q_z, Q_{\parallel}) |T_f|^2. \quad (2)$$

In Fig. 1 the scattering depth Λ is displayed as a function of the incident angle α_i and exit angle α_f . The inset shows the scattering geometry of a grazing incidence experiment.

The investigated sample was a flat plate with $[1\bar{1}0]$ orientation and dimensions of about $10 \times 10 \times 3 \text{ mm}^3$. The surface quality presents a rather serious problem. Bulk diffraction experiments showed a rocking curve with a broad intensity distribution with a width of about 0.1° – 0.5° , indicating the existence of several slightly misoriented crystallites. The as-grown crystal surface was too rough to observe any x-ray total external reflection. After the treatment described below, the sample showed a maximum reflectivity of only about 0.1%, which is very small compared to surfaces of high quality ($\gg 10\%$). The surface preparation started with a polishing procedure with Al_2O_3 powder down to $0.05 \mu\text{m}$, which led to an optically flat surface. Afterwards, the sample was sputtered with argon ions and annealed in different steps. The so-prepared sample was transferred under UHV conditions into a baby chamber with a cylindrical beryllium window, ion pump, and a liquid nitrogen cryostat. This UHV cell was taken to Hamburg and mounted on the diffractometer without breaking the vacuum.

The surface sensitive experiments were carried out us-

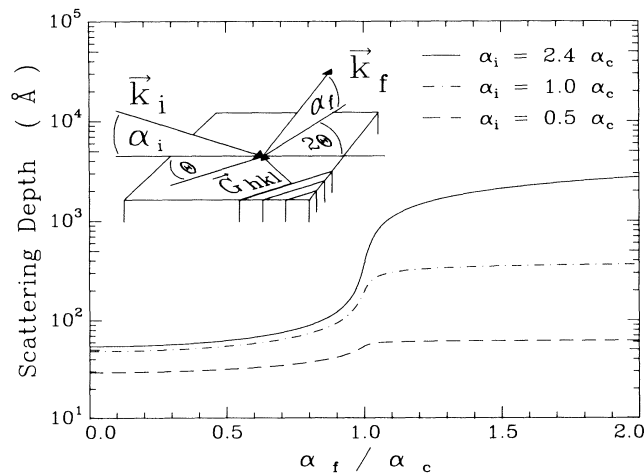


FIG. 1. Scattering depth Λ for NH_4Br ($\lambda=1.67 \text{ \AA}$). The inset shows the grazing incidence scattering geometry.

ing synchrotron radiation from the storage ring DORIS III on the wiggler beamline W1 (station R β WI) at HASYLAB, Hamburg. In particular, the temperature dependence of the $(\frac{1}{2}\frac{1}{2}1)$ superlattice reflection and the critical diffuse scattering in the vicinity of this reciprocal point were observed. By choosing different incident angles and detecting the α_f -resolved signal with a position sensitive detector the scattering depth was varied. The horizontal resolution in Q space was determined by the size of the slits (1 mm) and is about $3 \times 10^{-4} \text{ \AA}^{-1}$ at the lattice point $(\frac{1}{2}\frac{1}{2}1)$ for a wavelength of 1.67 \AA . The temperature stability was computer controlled within $\pm 0.08 \text{ K}$.

The surface Bragg reflections showed a relatively broad α_f profile compared to the expected line shape for a flat surface. This can be explained by the mosaic spread of the sample. By translating the sample along the surface the width of this curve varied significantly. To achieve best results, the part of the surface with the sharpest profile was chosen. But, unfortunately, different crystallites have different surface normals, which leads to some uncertainty in α_i and α_f . This limits the extent to which a depth profiling from the α_f -resolved measurements can be done. In the following, the analyzed data refer to exit angle integrated intensities while the scattering depth is only controlled by the angle of incidence.

In Fig. 2 some radial scans around the $(\frac{1}{2}\frac{1}{2}1)$ superlattice reflection are shown for temperatures *below*, *at*, and *above* T_c with a scattering depth of about 100 \AA . The analysis of the data has been done after separating the Bragg intensity (long-range order) from the diffuse critical scattering (short-range order). Well below T_c (the data are not shown here) only a narrow Gaussian shaped intensity distribution in Q space occurs along the

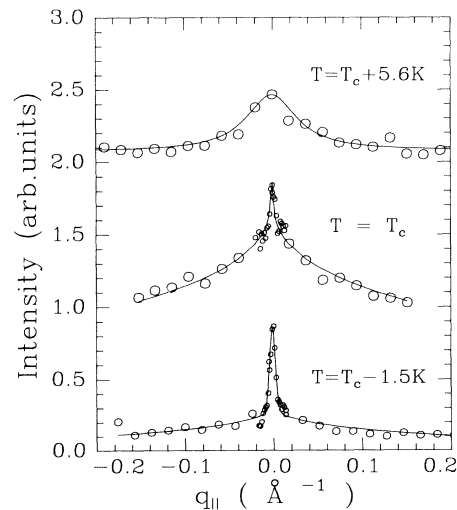


FIG. 2. Radial scans along $q_{\parallel} = Q_{\parallel} - G_{\frac{1}{2}\frac{1}{2}1}$ for a scattering depth of about 100 \AA at $T = T_c - 1.5 \text{ K}$, $T = T_c$, and $T = T_c + 5.3 \text{ K}$. The solid lines represent the fitted line shapes using the models given in the text.

in-plane momentum transfer $q_{\parallel} = Q_{\parallel} - G_{\frac{1}{2}\frac{1}{2}1}$. The superlattice reflections have a resolution limited full width at half maximum of about $5 \times 10^{-3} \text{ \AA}^{-1}$. Their intensity decrease reflects the decay of the long-range order. Close to T_c diffuse scattering from the critical fluctuations becomes visible below the Bragg peaks. These two components can be seen clearly in Fig. 2 for $T = T_c - 1.5 \text{ K}$. At T_c , the line shape is determined by a characteristic power law (see below); above T_c only the critical (diffuse) scattering remains.

To determine the temperature behavior of the order parameter below T_c we have analyzed the sharp long-range order component. The diffuse scattering was fitted by a Lorentzian line shape and subtracted. The integrated Bragg intensity follows a simple power law:

$$I \propto |1 - T/T_c|^\nu \quad (3)$$

with exponents $2\beta_1$ at the surface and 2β in the bulk. A log-log plot for a scattering depth of 100 \AA (Fig. 3) shows a crossover from bulk behavior to the predicted surface behavior at a temperature of about $1.8 \pm 0.5 \text{ K}$ below T_c . At low temperatures we find an exponent $\beta = 0.3 \pm 0.05$ (3D Ising, $\beta = 0.32$). Near T_c , the exponent changes to $\beta_1 = 0.8 \pm 0.1$. This must be compared with the theoretical value of $\beta_1 = 0.80$ in the ordinary case [14]. Below this crossover temperature the correlation length is small compared to the scattering depth $\Lambda \approx 100 \text{ \AA}$. At $T = T_c - 1.8 \text{ K}$ the increasing correlation length reaches a value of about 25 \AA (see below). This is in the range of the scattering depth and therefore the surface scattering starts to dominate [14].

Almost exactly at the critical temperature the line shape should follow another power law,

$$I \propto a - b|q_{\parallel}|^{\eta_{\parallel}-1}. \quad (4)$$

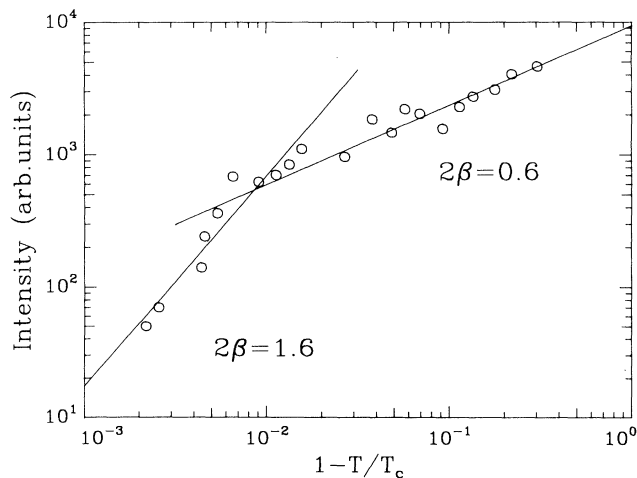


FIG. 3. Integrated Bragg intensity at $(\frac{1}{2}\frac{1}{2}1)$ for a scattering depth of about 100 \AA . The solid lines show the power laws for bulk and surface behavior with exponents $2\beta = 0.6$ and $2\beta_1 = 1.6$, respectively.

The best fit, as shown in Fig. 2, was achieved with an exponent $\eta_{\parallel} = 1.3 \pm 0.15$. In this fit a small contribution (about 10%) of Bragg scattering has been included. This may be due to a small spread of critical temperatures possibly from tetragonal strain at the surface. The derived exponent should be compared with the theoretical value of $\eta_{\parallel} = 1.48$ [14].

Above T_c there remains diffuse scattering due to the critical fluctuations. Though theory predicts a more complicated q_{\parallel} profile for the diffuse scattering in near-surface regions [15, 16], a Lorentzian line shape gave a reasonable fit to the data. This seems to be a good approximation when bulk behavior dominates that is not too close to T_c . From the temperature dependence of the peak width we deduced the decay of the correlation length using the power law

$$\xi = \xi_0^+ |1 - T/T_c|^{-\nu} \quad (5)$$

with a critical amplitude $\xi_0^+ = 4 \pm 0.5 \text{ \AA}$ and an exponent $\nu = 0.5 \pm 0.15$ (3D Ising, $\nu = 0.63$ [14]). The asymptotic surface behavior should be visible when the correlation length is in the range of the scattering depth. Assuming $\xi_0^+ = 2\xi_0^-$ the correlation length amounts to about 25 \AA at the crossover temperature below T_c . This value is less than the scattering depth, but possibly due to experimental uncertainties.

The temperature dependence of the diffuse scattering at $(0.49, 0.49, 1)$ is shown in Fig. 4 for two different incident angles, $0.5\alpha_c$ and $2.4\alpha_c$. The former corresponds to a maximal scattering depth of about 100 \AA (see Fig. 1) and is dominated by surface scattering; the latter shows bulk dominated behavior with a scattering depth of about 3000 \AA . Within error both curves peak at the same critical temperature. This indicates the presence

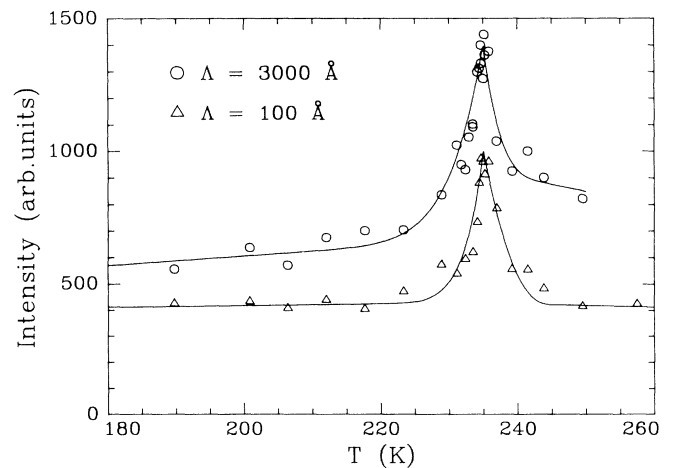


FIG. 4. Diffuse intensity at $(0.49, 0.49, 1)$ for $\alpha_i = 0.5\alpha_c$ ($\Lambda \approx 100 \text{ \AA}$) and $\alpha_i = 2.4\alpha_c$ ($\Lambda \approx 3000 \text{ \AA}$). Both curves peak at the same critical temperature $T_c = 235 \text{ K}$. (The solid lines are only a guide to the eye.)

TABLE I. Critical point exponents in near-surface regions. The experimental values for NH_4Br are compared with results from renormalization group theories [14].

Critical exponent	Theory (3D Ising, ordinary transition)	Experiment
β_1	0.80	0.80 ± 0.1
η_{\parallel}	1.48	1.3 ± 0.15
ν	0.63	0.5 ± 0.15

of an ordinary transition at the surface. The intensity follows a cusplike behavior as predicted by theory [15] which is quite different from the (resolution limited) divergence in the bulk. (The solid lines are only a guide to the eye.)

In conclusion, we have observed the near-surface critical behavior of a phase transition in a molecular crystal showing both an order-disorder aspect and a strong displacive component. Both the unchanged transition temperature $T_c^{\text{surf}} = T_c^{\text{bulk}}$ and the magnitude of the experimentally determined critical exponents are consistent with the predictions of an ordinary transition within the universality class of 3D Ising models (see Table I). Apparently, it is difficult to obtain a high surface quality of NH_4Br crystals. This limits both the counting statistics and the possibility of the depth profiling. While not providing a serious test of scaling relations, our data nevertheless are the first results for the near-surface transition of a molecular crystal. Further experiments near the tricritical point of ND_4Cl are planned.

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