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Surface phase transition close to a bulk tricritical point: An x-ray study of ND_4Cl

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Investigations of the near-surface critical behavior close to the bulk tricritical point of ND_4Cl single crystals are presented. The order parameter is expected to follow universal power laws with a temperature-dependent crossover from the bulk to the surface exponent. In contrast to the theory the measurements show an evidence for a surface layer with a constant nonvanishing order parameter. The thickness of this layer increases in temperature and seems to diverge at the critical temperature. The results disagree with the expected universal behavior of surface order parameters. [S0163-1829(99)07505-0]

I. INTRODUCTION

In the past, phase transitions of semi-infinite systems have been studied extensively. Depending on the special properties of the system, several universality classes of surface phase transitions were found with different critical behavior compared to the respective bulk transitions (see, e.g., Ref. 1). In the simplest case, the order parameter $m(z,T)$ decays exponentially in the direction perpendicular to the surface with the bulk value $m_b(T)$ for $z\rightarrow\infty$ and the surface order parameter value $m_1(T)\leqslant m_b(T)$ at $z=0$. For continuous phase transitions the decay length $\xi(T)$ of the order-parameter profile is temperature dependent and diverges at the critical temperature T_c.[2,3] Both $m_b(T)$ and $m_1(T)$, follow power laws. With the reduced temperature $\tau=T/T_c-1$ they are formulated as $m_b(T)\sim|\tau|^{\beta}$ and $m_1(T)\sim|\tau|^{\beta_1}$, with the universal critical exponents β and β_1. In general, β_1 differs significantly from β.[4] For example, the common Ising-model renormalization theory yields $\beta=0.325$ and $\beta_1=0.80$ in three dimensions for a one-component order parameter.[2,3]

Surface phase transitions, which are caused by the abrupt loss of the three-dimensional symmetry of a single crystal directly at the surface, are theoretically well understood and various detailed predictions were made (see, e.g., Refs. 1 and 5–7). Compared to the large body of work, which was done in the past concerning the theory of surface phase transitions, only few experimental studies exist which essentially have confirmed these predictions.[8–11] This is due to the difficulties which arise when surface phase transitions are investigated: (i) The systems have to be simple to fulfill all assumptions of the theory, (ii) the sample surfaces should be of high quality, and (iii) an adequate surface sensitive probe has to be found.

We present investigations on ND_4Cl. The bulk critical behavior of ammonium halides NX_4Y (with $X=\mathrm{H,D}$ and $Y=\mathrm{Cl,Br}$) is very well-known (see, e.g., Refs. 12 and 13). They exhibit an Ising-like orientational order-disorder transition. The two possible orientations of the ammonium tetrahedra correspond to the (pseudo-) spin-up and spin-down states, respectively. These pseudospins are coupled by a direct octupole-octupole interaction and an indirect octupole-dipole-octupole interaction via a displacement of the halide ions. The former interaction dominates in ammonium chlorides and leads to a ferro-ordered low-temperature phase. The latter is responsible for the antiferro-ordered phase, which appears in ammonium bromides at normal pressure.[12] In the disordered phase the ND_4^+ tetrahedra are flipping almost independently between the two alternative orientations. The order parameter of the ferro-ordered phase is given by

$$m=\frac{N_\uparrow-N_\downarrow}{N_\uparrow+N_\downarrow},$$

with the number $N_\uparrow$ of spin-up and $N_\downarrow$ of spin-down states.

For the ammonium halides a generalized phase diagram may be obtained which shows a bulk tricritical point (TCP).[14] The TCP can be reached by applying hydrostatic pressure. For ND_4Cl this pressure is only about 150 bar.[15] At normal pressure the transition is almost tricritical with a tiny first-order component.[16] The bulk TCP is well-known and has been investigated in the past with various methods.[15–17] Thus ND_4Cl seems to be an adequate system to investigate the surface phase transition at a bulk TCP.

II. GENERAL ASPECTS

An order-parameter profile $m(z,T)$ instead of a spatially constant value $m(T)$ is caused by the breaking of the translational symmetry of a crystal at the surface, i.e., at $z=0$.[1] Within the Landau theory an explicit form

$$m(z,T)=m_b(T)-[m_b(T)-m_1(T)]\exp[-z/\xi(T)],\quad (1)$$

may be obtained with a decay length $\xi(T)$. In the following, we will concentrate on x-ray scattering experiments to investigate this behavior and here mainly on grazing incidence diffraction (GID) (for a review of this method in connection with surface phase transitions see Dosch and references therein[9]). GID is a surface sensitive probe where the penetration depth Λ of the x rays is only on the order of 50,...,2000 Å in the total external reflection regime (grazing angles) and increases up to several microns for larger angles of incidence. Hence, the measured signal contains information averaged over the vertical distance Λ. Assuming an exponential decay of the signal inside the sample, the observed averaged order parameter profile by GID is

$$\langle m(z,T)\rangle_\Lambda=m_b(T)-\frac{m_b(T)-m_1(T)}{1+\Lambda/\xi(T)},\qquad (2)$$

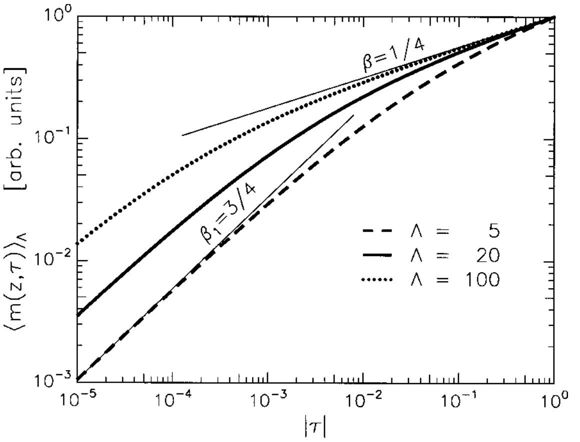

FIG. 1. Calculations of the crossover from the bulk to surface critical behavior, based on Eq. (2) with an universal power law $\xi = |\tau|^{-1/2}$ and the reduced temperature $\tau = T_c/T - 1$. Λ and ξ are given in units of lattice constants.

with the limit $\langle m(z,T)\rangle_\Lambda \rightarrow m_1(T)$ for $\Lambda \rightarrow 0$. Since $\xi(T)$ is almost zero for $T \rightarrow 0$ K and diverges at T_c for systems with continuous phase transitions, a smooth crossover from bulk to surface critical behavior is expected.[9] The crossover temperature is determined by Λ and the properties of $\xi(T)$.[10] For the particular case of ND_4Cl the universal critical exponents of a TCP $\beta = \frac{1}{4}$ (bulk) and $\beta_1 = \frac{3}{4}$ (surface) are expected.[1] Figure 1 depicts calculations which can directly be compared with the measurements.

In the past, the bulk order parameter of ND_4Cl has been determined by neutron-scattering experiments. The neutron-scattering length densities of Cl, N, and D atoms allow an investigation of the phase transition via distinct changes of the structure factor (see, e.g., Refs. 15 and 18). However, surface sensitive GID experiments with neutrons often lack both on intensity and collimation of the incoming radiation. Furthermore, very large samples are required. Therefore the present system cannot be investigated by neutron GID.

As mentioned above, $m(z,T)$ depends on the number of spin-up and spin-down oriented ND_4^+ tetrahedra, and thus on the distribution of the D atoms around the ND_4^+ molecule. As the x-ray structure factor is connected with the electron density, which is very small around the D atoms, a change of the order parameter of ND_4Cl leads to only very small changes in the Bragg intensities. Detailed calculations reveal that the expected intensity change of Bragg reflections is always less than 2%.[19] This change is too small for accurate surface phase-transition studies.

Furthermore, the phase transition shows no effect on the crystallographic structure of the lattice except for a loss of point symmetry (ferro-ordered phase: $P\bar{4}3m$, disordered phase: $Pm\bar{3}m$). Therefore the above-mentioned change of the structure factor is only visible at Bragg reflections *hkl* with $h,k,l \neq 0$ and no super lattice reflections will appear.

In summary, the surface phase transition of ND_4Cl can hardly be monitored via intensity measurements, even if high brillance synchrotron radiation would be used.

Another way to investigate the order parameter of ammonium halides is the measurement of the temperature dependence of the lattice constant, since the lattice constant of ND_4Cl couples to the order parameter: The octupole-octupole interaction between the ND_4^+ tetrahedra, which is responsible for the ordering process, leads to an additional mean-field-like potential $W[q,m(T)] = -61q^2[m(T)]^2R^6/(\pi\epsilon_0 a^7)$, where q is the effective charge of a D atom ($q \approx +1/4$), R is the distance of the D atoms from the central nitrogen atom, and a is the lattice constant.[19,20] The standard mean-field-like potential for ionic crystals is then given by

$$E(r) = -\frac{A}{r} + \frac{C}{r^\nu} + W[q,m(T)] \tag{3}$$

with the usual constants *A*, *C*, and ν (e.g., Ref. 21). The third term on the right-hand side of Eq. (3) yields an anomalous contraction of the lattice, which can explicitly be calculated as

$$\Delta a(T) \approx [m(T)]^2 \cdot c \tag{4}$$

with $c \approx 0.01$ Å. Experimentally, this was confirmed by x-ray scattering measurements on bulk ND_4Cl.[19,20] More quantitatively, Eq. (4) means that an order-parameter dependent contraction with a maximum of 0.3% of the lattice constant $[a(T_c) \approx 3.86$ Å$]$ is expected.

In the present study we have used this effect for the measurement of $m(z,T)$: The temperature-dependent shift of Bragg positions as a function of the penetration depth of the x rays was monitored by GID experiments. The penetration depth Λ of the x rays can be controlled by the incident and exit angle. It is well known that this configuration covers a range of $\Lambda = [10^2,\ldots,10^5]$ Å.[9] Thus the order parameter profile can be measured by choosing adequate penetration depths and applying Eq. (2) to extract the critical exponents. However, it should be pointed out that by measuring Bragg positions instead of intensities no *direct* access to order-parameter fluctuations is possible.

III. SAMPLES AND EXPERIMENTAL DETAILS

A single crystal of ND_4Cl of size $(5\times5\times5)$ mm^3, which was approximately 98% deuterated, has been used for the measurements. It was grown by B. N. Brockhouse, M. Collins, and J. Garrett, McMaster University, Canada and is a mosaic crystal consisting of crystallites of about 1 micron diameter. The mosaicity was determined to be 0.035°.

Since it is not possible to cleave ND_4Cl crystals along crystallographic planes to obtain atomically flat surfaces,[22,23] the sample was prepared by sawing along the [100] direction and by applying subsequent polishing steps. After the preparation the surface had a miscut of about 0.1° and a macroscopic curvature with a radius of about 10 m.

The microscopic quality of the surface was checked by x-ray reflectivity and diffuse scattering measurements (see Fig. 2). To obtain the rms roughness σ_s, the in-plane correlation length ξ_s, and the Hurst parameter h_s (fractal model; see, e.g., Ref. 24) the standard way to analyze the data was not applicable. Usually σ_s is determined by subtracting the diffuse scattering from the reflectivity data and fitting the true specular reflectivity. In our case this procedure fails, because the whole signal is almost dominated by the diffuse scattering (see Fig. 2, right). Therefore the reflectivity and the diffuse scattering measurements have been refined simul-

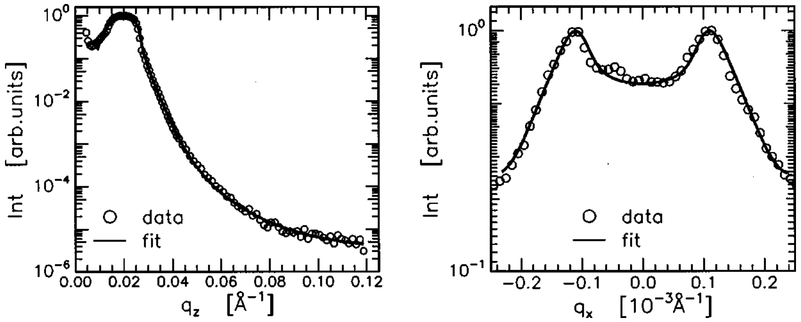

FIG. 2. Left: Reflected intensity vs perpendicular wave-vector transfer q_z of the ND_4Cl surface. Right: Transverse scan along q_x at constant $q_z = 0.0456$ Å^{-1}. The lines are fits of the data.

taneously: The calculation of the reflectivity contains the true specular part and the diffuse scattering at the specular position. The same parameters were simultaneously used for the explanation of the transverse scan. This method has been described in some more detail in a paper by Schlomka *et al.*[25] For the ND_4Cl sample the values $\sigma_s = (67 \pm 5)$ Å and $h_s = 0.31 \pm 0.15$ are obtained. The fit is almost insensitive to a change of ξ_s, which was set to 1000 Å. These parameters indicate that a jagged surface with a rather large surface roughness is present.

Obviously, the obtained surface is less perfect than those used in previous studies where mainly metals and alloys were investigated.[9,26] This finding is not suprising, because it turns out to be extremely difficult to prepare smooth and clean surfaces of ND_4Cl crystals. This is not only due to the softness of the samples, which makes it impossible to cleave a crystal. Additionally, any contact with water or fluids containing H atoms has to be avoided since ND_4Cl tends to exchange the D atoms with H atoms. Furthermore, the crystals cannot be annealed because strong sublimation takes place for temperatures higher than 350 K. The effect of the large roughness σ_s on the surface phase transition will be discussed in Sec. IV.

The sample was fixed onto a copper holder using a glue with high thermal conductivity (Polytec EPO-TEK417). The temperature sensor, a platinum resistor (Heraeus Pt100), was placed in direct neigborhood of the sample. The copper holder contains a heating wire (Philips 1NcI05) and was located inside a high-vacuum chamber (spherical Be can by Degussa), which was evacuated to a pressure of 10^{-9} mbar and connected to a He closed cycle cryostat (Leybold Rw4000). The temperature was set by a controller (Lakeshore 330) and was varied in the range 190–300 K with a stability of 0.01 K over several hours. The setup allows bulk as well as surface sensitive measurements. For further details see Ref. 19.

The x-ray experiments were done at the beamlines BW2 and W1.1 at the synchrotron radiation source HASYLAB (Hamburg, Germany) with a photon energy of 8 keV. A position sensitive detector (PSD) was placed at the position of the 100 GID reflection. The temperature-dependent shift of the Bragg reflection was monitored without moving any motor, only by analyzing the shift of the peak in the PSD spectra. With this method the change of the lattice constant $\Delta a(T)$ was measured very accurately [the error of $\Delta a(T)$ is on the order of 5×10^{-4} Å]. For scans close to the 100 bulk Bragg reflections the resolution was $\delta q_{\mathrm{res}} = 0.25 \times 10^{-3}$ Å. Because of geometrical effects the GID reflections are much broader than the resolution function. The respective full width at half maximum is determined by the footprint of the primary beam on the sample surface.

Four different nominal penetration depths ($\Lambda \in [50,1000,4000,10\,000]$ Å) were chosen for the GID measurements. The values of the incident and exit angles corresponding to these penetration depths depend on the photon energy and the sample properties[9] and were in the range of 0.05,...,0.5° for the present study.

IV. MEASUREMENTS AND RESULTS

The bulk phase transition has been characterized before the surface sensitive measurements were performed. We found a critical temperature of $T_c = (248.94 \pm 0.30)$ K. The error is caused by the fact that absolute temperatures cannot be measured more accurately with our setup. However, the error in determining temperature differences was only 0.01 K.

As mentioned above the order-parameter profile $m(z,T)$ of ND_4Cl was analyzed using the temperature and penetration depth dependent shift of the 100 surface Bragg position. Typical data are depicted in Fig. 3. The reflections exhibit an integrated intensity of about 10 counts/s, corresponding to less than 10^{-8} of the primary flux.

The left part of Fig. 4 shows the temperature dependence

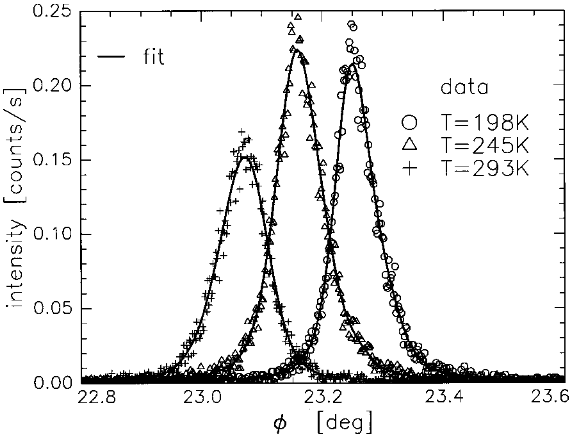

FIG. 3. Examples of GID measurements of the 100 surface Bragg reflection. The position of the maxima shift with temperature. ϕ is the scattering angle, lines are fits with a combination of a Gaussian and a Lorentzian.

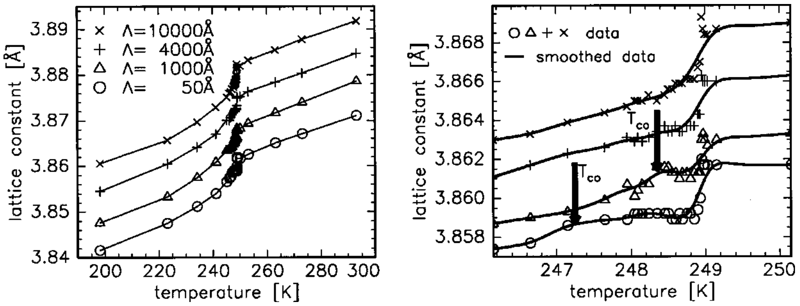

FIG. 4. Depth dependent values of the lattice constant $a(T)$. The left part shows the overall behavior, the right is a magnification of the region close to T_c. The arrows mark the crossover temperature T_{co} at which the general curvature changes. The lines are guides to the eye. For clarity the curves for each Λ are shifted with respect to each other.

of the lattice constant $a(T)$ as obtained from the measurements. Apart from the usual thermal contraction an additional contribution due to the coupling of $m(z,T)$ with $a(T)$ [see Eq. (4)] is present. The right-hand side of the illustration displays a magnification of the region around T_c and shows that the temperature dependence of the lattice constant close to the transition temperature T_c depends significantly on the penetration depth. For the two smaller penetration depths $\Lambda = 50\,\text{Å}$ and $\Lambda = 1000\,\text{Å}$ a temperature T_{co} can be identified (marked by arrows), which indicates a kind of crossover. This feature is not visible for the larger penetration depths.

For a more quantitative analysis a $\log_{10}$-$\log_{10}$ plot of the reduced lattice constant (the elastic strain e_1, see Ref. 27) versus the reduced temperature $\tau = T/T_c - 1$ is given in Fig. 5. The reduced lattice constant was determined by subtracting the linear thermal contraction, which was calculated by linear regression using the data points with $T > 252\,\text{K}$. The data of a bulk measurement at the 311 Bragg reflection are included to illustrate the penetration depth dependent behavior. As e_1 depends quadratically on $m(z,T)$ [see Eq. (4)], this result can be directly compared with the expected theory shown in Fig. 1.

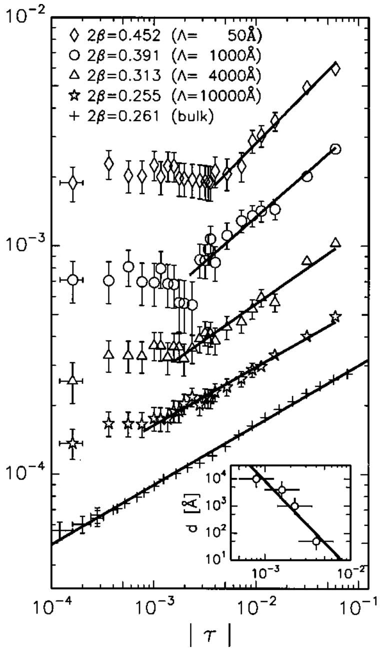

FIG. 5. $\log_{10}$-$\log_{10}$ representation of the reduced lattice constant (strain e_1) versus the reduced temperature $\tau = T/T_c - 1$ (symbols are data, lines are fits). Included is an example for a bulk measurement at the 311 reflection. The crossover temperature T_{co} is given by the left end of the lines. The inset shows the thickness d of the modified surface layer (see text) vs the reduced temperature. Error bars are shown if they exceed the size of the symbols.

Before discussing the data of the surface sensitive measurements it should be mentioned that the bulk investigations did not yield the tricritical value of 1/4 for β. This is well known for ND_4Cl and in the past often observed experimentally.[15,16,21] The reason is the coupling of the order parameter with the lattice constant. The ordering potential $W[q,m(T)] \sim 1/a^7$ depends on the lattice constant (as shown above) thus a modification of the critical behavior, essentially a self-amplification of the ordering process near T_c, is expected. By introducing a rescaled critical temperature $T_\chi = T_c[1 - \Delta a(T)/a(T_c)]^7$, the critical behavior of ND_4Cl was explained in a previous study (see Ref. 20). However, as the error bars of the surface sensitive measurements are much larger than those for the bulk measurements this ‘‘rescaling’’ is not visible. Thus we used the standard procedure of data analysis to determine the critical exponents which is basically a linear regression on a $\log_{10}$-$\log_{10}$ scale.

The data corresponding to $\Lambda = 10^4\,\text{Å}$ almost match the known bulk behavior since $\Lambda \gg \xi$ holds for all temperatures. For $\Lambda = 4000\,\text{Å}$ a ‘‘crossover’’ appears that is even more clearly visible for the smaller penetration depths $\Lambda = 1000\,\text{Å}$ and $\Lambda = 50\,\text{Å}$. The crossover temperature T_{co} strongly depends on Λ: The smaller Λ the larger is the distance between T_{co} and T_c. In the region $T_{\mathrm{co}} < T < T_c$ the lattice constant $a(T)$ remains constant within the error bars. This finding is incompatible with a smooth order-parameter profile suggested by the standard theory of universal critical behavior, which is mentioned above and discussed in detail in Ref. 9. Instead, a profile with rather abrupt changes of $m(z)$ is found that may be interpreted as a layer at the surface with the following properties: (i) The thickness $d(T)$ of this layer drastically increases when approaching T_c from below. (ii) The order parameter is constant within this layer but does not vanish (see Fig. 4). In this picture T_{co} marks the temperature above which $d(T)$ significantly exceeds Λ. The data yield $d(T_c - 1.0\,\text{K}) \approx 50\,\text{Å}$, $d(T_c - 0.6\,\text{K}) \approx 1000\,\text{Å}$, $d(T_c - 0.4\,\text{K}) \approx 4000\,\text{Å}$, and $d(T_c - 0.15\,\text{K}) \approx 10^4\,\text{Å}$ (see inset of Fig. 5). It should also be noted that these values, except for the first, are much larger than the measured surface roughness σ_s. However, the surface roughness and the curvature of the surface yield a rather large uncertainty in the precise determination of the penetration depths. This fact and the error bars of the data lead to a total error of almost 50% for the $d(T)$ values. A power-law fit yields $d(\tau)\sim|\tau|^{-\kappa}$ with $\kappa = 3.3\pm 0.8$ (see inset of Fig. 5). If we tentatively identify the thickness $d(T)$ with the decay length $\xi(T)$ given by Eq. (1) the exponent $\kappa = 3.3\pm 0.8$ is far above all known values of critical exponents ν (e.g., $\xi\sim|\tau|^{-\nu}$ with $\nu = 0.5$ at the bulk TCP). Furthermore, an additional systematical effect can be evaluated from the data. The smaller the penetration depth Λ the larger is the deviation from the bulk critical behavior, which is expected to appear for $T < T_{\mathrm{co}}$. In summary, the behavior described above differs completely from all predictions of the theory which are plotted in Fig. 1.

It is well known for several other systems, that a surface region with enhanced ordering/disordering may appear for temperatures close to the transition temperature. Examples are near-surface freezing of alkanes and alkane mixtures, surface melting of ice, or layering at the surface of liquid metals.[26,28–30] The layer described in this paper may also be interpreted as a kind of ‘‘frozen spin’’ layer. But this is highly speculative because no such ordering has been reported for ammonium halides so far.

As pointed out in Sec. III, the surface of the sample was not perfect. In particular the surface roughness of $\sigma_s = 67$ Å may cause modifications from the expected surface behavior at least for small penetration depths. But it turned out that the GID reflections measured with a nominal penetration depth of only $\Lambda = 50$ Å were not broadened or shifted compared to those which correspond to the bulk value of $\Lambda = 10^4$ Å. Thus the roughness does not lead to ‘‘dead layers’’[9] with a destroyed crystal structure. In addition, it is theoretically predicted, that for ‘‘ordinary transitions’’ surface roughness has a negligible effect, if the decay length $\xi(T)$ of $m(z,T)$ is much larger than the roughness (for $T\to T_c$).[31,32] This suggests that the observed effect is real and not caused by imperfections of the surface of the investigated crystal.

Since we have not measured directly at the TCP another possible source for the unexpected behavior of the sample may be the remaining tiny discontinuity (first order component) at T_c. However, the surface phase transition of NH_4Br (with a comparable discontinuity in the phase diagram) has successfully been studied.[11] Furthermore, one may also speculate about the following: As mentioned above for the bulk system the secondary order parameter, which is the temperature-dependent variation of the lattice constant, yields the same critical exponent β as the primary order parameter (the averaged orientation of the ND_4^+ tetrahedra).[20] In the near-surface region this may not be true and a more complicated relationship between $m_1(T)$ and $a(T)$ may exist. Here we hope that our measurements will stimulate further theoretical work.

V. SUMMARY

The surface phase transition behavior of a tricritical system was investigated with x-ray GID experiments. A ND_4Cl single crystal with an Ising-like order-disorder transition, which is very close to a tricritical transition at normal pressure, and $T_c = (248.96\pm 0.3)$ K was investigated. A temperature-dependent order-parameter profile $m(z,T)$ is expected with a diverging decay length $\xi(T)$ for $T\to T_c$. Depending on the penetration depth Λ of the x rays a crossover from the bulk behavior to surface critical behavior should appear at a crossover temperature T_{co}. Our measurements are incompatible with these predictions. They may be interpreted in a different manner by assuming a layer with a temperature-independent finite order parameter. The thickness $d(T)$ of this layer increases with $T\to T_c$ and seems to diverge at T_c. Assuming a power law $d(\tau)\sim|\tau|^{-\kappa}$ an exponent of $\kappa = 3.3\pm 0.8$ is found which does not correspond to any known critical exponent. An explanation of our data within a microscopic model is not yet available. However, we would like to mention that the assumption of a layer with a temperature-independent finite order parameter is highly speculative and we hope that the presented data may be the base of further theoretical developments.

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