

Near-surface tricritical behavior of $V_2H(010)$ at the β_1 - β_2 phase transition

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We present results of an x-ray grazing-incidence diffraction experiment on a $V_2H(010)$ surface. The temperature dependence of the in-plane ($h/2 \ 0 \ -h/2$) superlattice reflections discloses the surface critical behavior across the β_1 - β_2 phase boundary. The influence of a nearby bulk tricritical point on the expected values for the critical exponents is briefly discussed. Using the depth sensitivity of evanescent scattering and by a proper subtraction of critical diffuse intensity, we determined the surface critical exponent β_{surf} . A remnant Bragg contribution above the critical temperature, however, complicates the evaluation of other surface exponents associated with the critical diffuse scattering. We speculate that the origin of this effect is associated with the surface oxide layer necessarily present on the (hydrogen-loaded) metallic crystal. [S0163-1829(97)01425-2]

The possibility of using x-ray scattering to probe surface transitions has stimulated several experiments which observed a modified surface critical behavior.^{1,2} In order to be sufficiently depth sensitive, it is necessary to take advantage of the unique geometry in which x-ray scattered intensities are collected in grazing incidence geometry for both incident (α_i) and exit (α_f) angles. Earlier works focused either on first-order transitions,¹ where surface-induced disorder may be observed, or a continuous transition² in which an entire set of specific surface critical exponents³ could be determined. However, there has been no experimental work on the crossover from a continuous to a first-order transition. It is therefore a natural extension of this prior work to focus on the surface transition in the presence of a bulk tricritical point. We report here a synchrotron-based x-ray study of the surface critical behavior of V_2H across the β_1 - β_2 phase boundary, in which the character of the transition changes on varying the concentration of hydrogen.

Tricritical systems are usually described by a mean-field model for the free energy⁴

$$F = (1/2!) t \phi^2 + (1/4!) g \phi^4 + (1/6!) w \phi^6, \quad (1)$$

where ϕ is the long-range-order (LRO) parameter, $w > 0$ and $t = (T - T_c)/T_c$ is the reduced temperature. On changing the parameter g this model simulates different bulk transitions (at $t=0$) across a critical point ($g > 0$), a tricritical point ($g=0$), and a two-phase coexistence region or a discontinuous boundary ($g < 0$). For $g=0$ one obtains $\langle \phi \rangle \propto |t|^\beta$ for $T < T_c$, with $\beta_{\text{bulk}} = 0.25$.⁵ For a truncated solid a modified critical behavior is usually seen near the surface.⁶ Different types of behavior may be observed, but the most common and physically motivated is the ordinary transition,⁶ in which near the surface the order parameter exhibits a modified scaling behavior against a reduced temperature, with $\beta_{\text{surf}} = 0.75$ for a bulk tricritical point.⁷

Below T_c , x-ray scattering can probe an order-disorder transition through a measurement of the integrated intensity of a superlattice Bragg reflection, which is proportional to the square of the order parameter $I_{\text{Bragg}} \propto \langle \phi \rangle^2$. In the ordered β_1 phase of V_2H the hydrogen atoms are located in selected interstitial octahedral sites of every other (pseudo) body-centered tetragonal (bct) (10-1) plane, as shown in the inset of Fig. 1. In the β_2 phase above T_c the hydrogen atoms are,

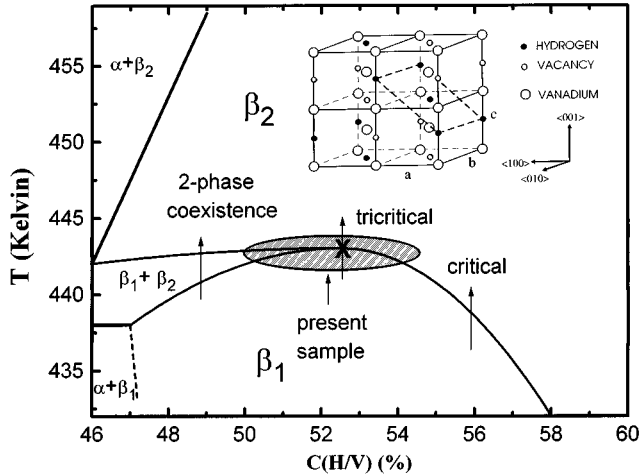


FIG. 1. Vanadium-hydrogen alloy phase diagram close to the atomic concentration $C(H/V)=50\%$ (Ref. 8). On varying C the character of the β_1 - β_2 phase transition changes from critical ($C \gg 50\%$) to tricritical ($C \cong 51\%$). The exact position of the tricritical point (marked with an \times) is not known (the shaded area indicates the region where it may be located). For $C \leq 50\%$ we observe a two-phase coexistence region near T_c . The inset shows the structure of ordered β_1 - V_2H . The hydrogen atoms are located in selected octahedral sites of every other $(10-1)$ plane, displacing the vanadium atoms from their average positions in the bct lattice.

on average, distributed randomly over the two sets of sites in Fig. 1 (inset) leading to a disordered bct structure. The transition to the β_2 phase is probed by the vanishing of the $(h/2\ 0\ -h/2)$ reflections which originate in the ordered hydrogen-induced vanadium displacements in the bct lattice. Bulk x-ray scattering experiments^{8,9} have revealed that the critical exponent $\beta_{\text{bulk}}=0.15$ is considerably lower than expected for any of the three-dimensional critical systems. It was concluded from the V-H phase diagram (Fig. 1) that the presence of a nearby tricritical point modifies the values of the critical exponents.⁸ Although the exponent β_{bulk} disagrees with its predicted theoretical value (0.25), a lower value for this exponent is common in tricritical systems¹⁰ and reflects logarithmic corrections which are difficult to account for in the fitting procedure.

In the case of a surface x-ray experiment the integrated intensity of a superlattice reflection is given by¹¹

$$I(q_z) \propto |T(\alpha_i)|^2 |T(\alpha_f)|^2 e^{-2M} \left| \int_0^\infty \phi(z) e^{-z/\Lambda} e^{-i\text{Re}(q_z)z} dz \right|^2, \quad (2)$$

where q_z is the out-of-plane momentum transfer, $T(\alpha_i)$ and $T(\alpha_f)$ are Fresnel transmission functions and $\Lambda=1/\text{Im}(q_z)$ is the penetration depth of the x-ray beam. $2M \equiv \{[\text{Re}(q_z)]^2 - 1/\Lambda^2\} \sigma + 2L/\Lambda$, and is analogous to a Debye-Waller factor which incorporates the effect of the surface roughness σ together with a cap layer of thickness L which does not contribute to the scattering. $\phi(z)$ is the depth-dependent order parameter.

For the present experiment a vanadium single-crystal plate, with $\langle 010 \rangle$ normal to the surface, and a very low mosaic spread ($\sim 0.03^\circ$), was loaded with purified H_2 at

650°C , followed by a slow cooling. The V_2H crystal exhibited a single-crystalline structure with two domains reflecting the equivalent (101) and $(10-1)$ hydrogen-induced ordering directions. After loading, the mosaic spread increased to $\sim 0.12^\circ$. The atomic H-V ratio was later determined by residual pressure and weight-loss measurements on heating to be $52.3 \pm 0.2\%$. We note that it is difficult to obtain a sample with a hydrogen concentration at the exact location of the tricritical point.

An in-house bulk x-ray measurement of the temperature dependence of the $(4\ 0\ -4)$ and $(5/2\ 0\ -5/2)$ reflections revealed that the crystal traverses a narrow ($\beta_1 + \beta_2$) two-phase region of approximately 0.3 K, which guaranteed the proximity to the tricritical point. The value of the exponent β_{bulk} was obtained from a fitting of the temperature behavior of the $(5/2\ 0\ -5/2)$ reflection against reduced temperature $I_{\text{Bragg}} \propto |t|^{2\beta_{\text{bulk}}}$, and varied from 0.13 (for a fixed T_c , obtained from the peaking of the critical diffuse intensity) to 0.18 (by allowing T_c to vary as a free fitting parameter, equivalent to correcting for the small discontinuity across the phase boundary). In contrast with a prior study¹² that revealed the absence of critical fluctuations on crossing a wide (2 K) coexistence region (lower H concentration), the present crystal exhibits pronounced critical diffuse scattering associated with a nearly continuous transition.

For the surface-sensitive experiment another piece of the same crystal plate was carefully prepared with a $\langle 010 \rangle$ normal to the surface (the pseudotetragonal axis is along $\langle 001 \rangle$). The crystal was polished with a $3\mu\text{-Al}_2\text{O}_3$ solution and later by a SiO_2 suspension which produced a mirrorlike and optically flat surface. A final electrochemical procedure removed the damaged layers produced by the polishing, but added an oxide layer to the surface and a waviness equivalent to $\Delta\alpha_f=0.09^\circ$. An analysis of the surface evanescent α_f profiles yielded $\sigma=7\text{ \AA}$ for the surface roughness and $L=50\text{ \AA}$ for the thickness of the oxide cap layer.

The crystal was taken to beamline X2A at the National Synchrotron Light Source and mounted on a six-circle diffractometer using a monochromatic x-ray beam ($\lambda=1.3625\text{ \AA}$, which set the critical angle of total reflection to $\alpha_c=0.29^\circ$). The scattered intensities were collected by a position-sensitive proportional counter mounted perpendicular to the scattering plane. Since the hydrogen was confined to the vanadium lattice by the oxide layer no further surface treatment was done to avoid any change in the hydrogen concentration, but the crystal was kept in a vacuum of 10^{-7} Torr throughout the experiment to avoid any further oxidation.

In order to determine the near-surface long-range order near $T_c=447\text{ K}$ we have measured the $(5/2\ 0\ -5/2)$ x-ray reflection for two different incident angles α_i with an open detector technique using rocking ω scans (over a range of $\pm 0.6^\circ$ in steps of 0.024°), which essentially integrated over all Bragg and diffuse scattering. In Fig. 2 we present the α_f - and ω -integrated intensity for $\alpha_i=1.14\alpha_c$ [the position of maximum intensity as $f(\alpha_i)$] and $1.62\alpha_c$, corresponding to penetration depths of 120 and 1000 \AA , respectively.

For an accurate determination of the asymptotic behavior of the integrated Bragg intensity below T_c , one must first subtract the contribution from critical diffuse scattering, which is most intense exactly at T_c . We have evaluated the

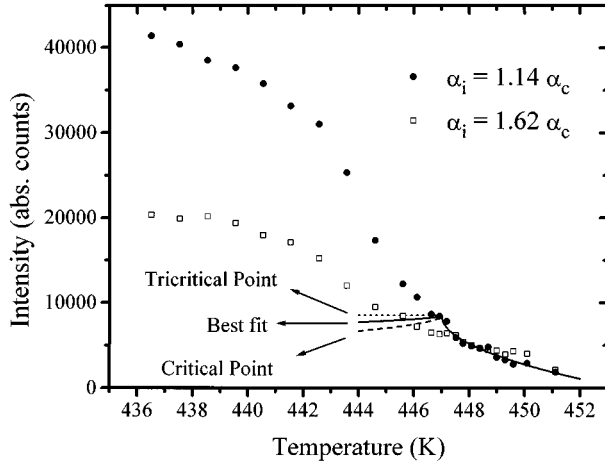


FIG. 2. Determination of the diffuse contribution below T_c from the intensity obtained in the disordered phase. Notice the good quality of the fit in the disordered phase, in which the predicted value for $\gamma_{1,1} = -0.5$ was used. The best fit refers to the results obtained from the fitting of the remaining Bragg intensity below T_c , shown in Fig. 3.

diffuse contribution below T_c using the total integrated intensity in the high temperature phase as a reference. As is known,¹³ the near-surface critical diffuse scattering exhibits a nondivergent temperature dependence given by $I_{\text{diff}}(t) = A_0(1 + A_1^+ |t|^{-\gamma_{1,1}} + A_2^+ |t| + \dots)$ where A_1^- and A_1^+ are different amplitudes associated with the low- and high-temperature phases ($A_1^+ < 0$) and $\gamma_{1,1} = -0.5$ for a tricritical system. The diffuse intensity in the high-temperature phase is well fit with $A_0 = 8718$ and $A_1^+ = -0.398$ (fitted as free parameters) and setting $A_{i \geq 2} = 0$ (see Fig. 2).

The diffuse contribution in the low-temperature phase [$I_{\text{diff}}(t) = A_0(1 + A_1^- |t|^{-\gamma_{1,1}})$] was determined from A_1^+ and the theoretical values of A_1^-/A_1^+ taken from the literature.¹⁴ We varied the value of A_1^-/A_1^+ from 0.32 (expected for a critical point) to 0 (tricritical point), subtracted the obtained curve from the overall intensity seen in Fig. 2, and fitted the remaining Bragg intensity to the law $I_{\text{Bragg}} = I_0 |t|^{2\beta_{\text{surf}}}$.

In Fig. 3 we present the asymptotic behavior of the remaining Bragg intensity against reduced temperature on a log-log scale where the best fit was obtained for $10^{-2} > |t| > 10^{-3}$ with $\beta_{\text{surf}} = 0.76 \pm 0.07$ and $A_1^-/A_1^+ = 0.12$. A clear change from bulk-dominated to surface-dominated critical scattering is seen at $|t| = 10^{-2}$. In principle, this crossover should occur when Λ is comparable to the correlation length, and we become sensitive to the near-surface order parameter, but we do not have direct evidence of this. Nonetheless, the results of Fig. 3 provide us with strong evidence of a *surface ordinary transition* in this material.

We turn now to radial scans parallel to the surface near T_c , where we observed a superposition of critical diffuse scattering and a remnant Bragg contribution [for the evaluation of β_{surf} , described above, this remnant Bragg contribution was not subtracted from the diffuse scattering because it amounted to less than 20% of the total intensity near T_c , integrated over the vicinity of the $(5/2\ 0\ -5/2)$ reflection, and did not exhibit a strong temperature dependence]. In Fig.

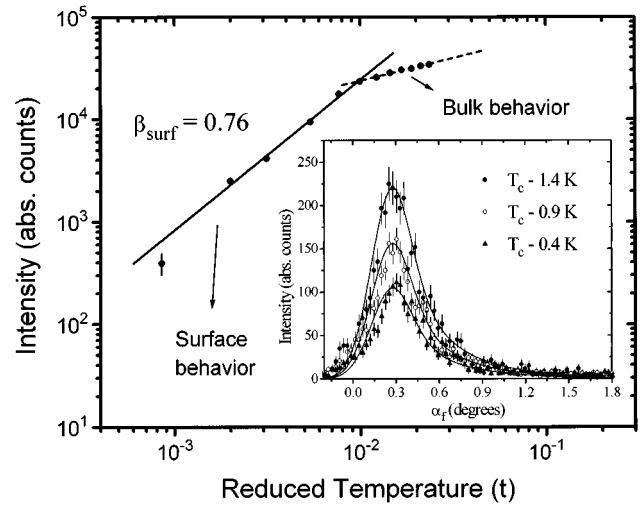


FIG. 3. Asymptotic behavior of the α_f -integrated Bragg scattering for $\alpha_i = 1.14\alpha_c$. Notice the crossover from a bulk- ($t > 10^{-2}$) to a surface-dominated ($t < 10^{-2}$, $\beta_{\text{surf}} = 0.76$) regime of critical scattering (the penetration depth is $\Lambda = 120\ \text{\AA}$). The inset shows α_f profiles for $\alpha_i = \alpha_c$, which were fit using Eq. (2) but assuming a depth-independent order parameter; this also included the effects of waviness of the surface, its roughness $\sigma = 7\ \text{\AA}$ and an oxide cap layer ($L = 50\ \text{\AA}$). Note that the intensity at small α_f falls below the fit curve indicating an enhanced disorder at the surface.

4 we present a (α_f -integrated) radial scan of the $(5/2\ 0\ -5/2)$ reflection along the $(10\ -1)$ direction at $\alpha_i = 1.6\alpha_c$ and $t = -9 \times 10^{-4}$ ($T = 446.6\ \text{K}$). We have fitted the profile at $\alpha_i = 1.6\alpha_c$ using the predicted law for surface critical diffuse scattering.¹¹ $I_{\text{diff}}(\mathbf{q}, T_c) \cong B_0(1 + B_1 |\mathbf{q}|^{\eta_{\parallel}})^{-1}$ [where $|\mathbf{q}|$ is the distance to the $(5/2\ 0\ -5/2)$ peak position and the coefficient B_1 is depth dependent] and allowed for a small Bragg contribution. The profile was convoluted with the instrumental resolution of $0.019\ \text{\AA}^{-1}$ measured at $T_c - 8.5\ \text{K}$. We obtained $\eta_{\parallel} = 1.07$, which obviously cannot be correct (if compared with the predicted value of $\eta_{\parallel} = 2.0$ for a tricritical

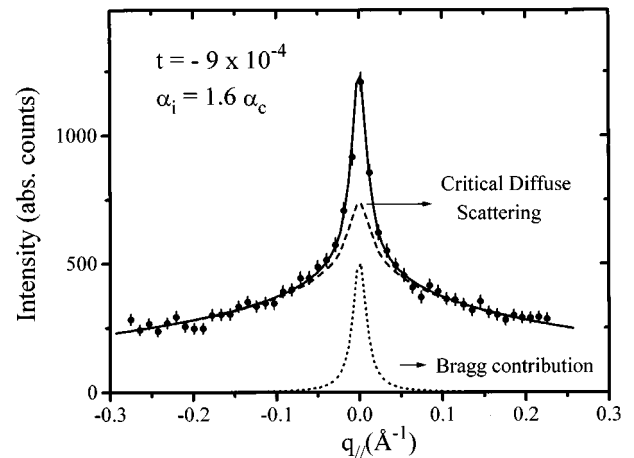


FIG. 4. Least-squares fit to a radial scan of the $(5/2\ 0\ -5/2)$ reflection at $t = -9.0 \times 10^{-4}$ and $\alpha_i = 1.6\alpha_c$ (see text). The variable q_{\parallel} refers to the distance to the $(5/2\ 0\ -5/2)$ reflection in reciprocal space ($|\mathbf{Q}_{5/20-5/2}| = 7.043\ \text{\AA}^{-1}$).

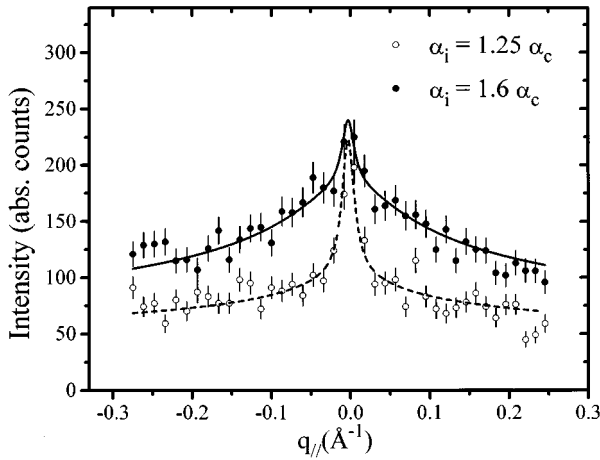


FIG. 5. Comparison between radial scans at $T = T_c + 6.0$ K for $\alpha_i = 1.25\alpha_c$ ($\Lambda \cong 200$ Å, open circles) and $\alpha_i = 1.6\alpha_c$ ($\Lambda \cong 1000$ Å, full circles). Notice the absence of diffuse scattering for a shallower angle, evidencing the weakening of critical fluctuations on approaching the surface.

point) since we are working above the critical angle ($\Lambda \sim 1000$ Å), and we are probing mainly bulk critical behavior.

The contrast between bulk (short-range order) and surface (long-range order) profiles becomes even more evident at $T = T_c + 6.0$ K as shown in Fig. 5. The profile obtained for $\alpha_i = 1.6\alpha_c$ was fitted by the Lorentzian line shape expected for *bulk* critical diffuse scattering¹¹ and is clearly the result of the remaining critical fluctuations above the critical temperature. At $\alpha_i = 1.25\alpha_c$ the (weak) surface density fluctuations near T_c have vanished and only a small (but persistent) LRO is left.

Two remarks should be made concerning the possible reasons for the presence of the remaining LRO: (i) the oxide layer produced by the electropolishing procedure certainly

imposes some stress on the metal-oxide interface and consequently it could act as an applied field at the metallic surface; (ii) because of the small (0.3 K) discontinuity in the bulk phase boundary, the surface thermodynamics, i.e., phase coexistence, of the material could be altered causing the presence of a surviving β_1 phase at the interface above the bulk T_c . This effect, however, is not accounted for by any of the available theories for surface critical behavior. It is, nonetheless, reminiscent of the ordered “skin” observed by several authors¹⁵ above critical points in various phase transitions which is often referred to as a second length scale. Here it would seem clearly to be associated with the surface oxide.

In summary, the near-surface disordering process of V_2H was studied by x-ray evanescent scattering and, in spite of the presence of a cap layer which did not contribute to the scattering, could be understood as a surface ordinary transition in the presence of a bulk tricritical point. This was evidenced by the measured critical exponent $\beta_{\text{surf}} = 0.76 \pm 0.07$. Both Bragg and diffuse scattering results agree qualitatively with this picture and they constitute the first experiment performed on the crossover from a continuous to a discontinuous transition. The presence of an interface imposes a remnant *surface* Bragg peak above T_c which interferes with the assessment of other critical exponents. The critical fluctuations near the metal-oxide interface are weakened, possibly due to the stress imposed by the oxide cap layer. We observed a pronounced diminishing of the diffuse scattering coming from the near-surface region of the crystal, as compared with the bulk where these fluctuations were shown clearly to be present.

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