Change from a bulk discontinuous phase transition in $V_2H$ to a continuous transition in a defective near-surface skin layer


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Introduction

We report here on a study of the effect of defects on the order-disorder $\beta_1\beta_2$ phase transition in the interstitial alloy $V_2H$, which is believed to be a system analogous to a metastable. Since defects exist in almost any real system, the understanding of their influence on phase transitions is crucial for a comparison with experiments. Recent theoretical work has revealed that a system undergoing a discontinuous transition can be converted to a continuous transition if quenched random bonds (see e.g., [2, 3] and refs. therein) or random fields (see [4] and refs. therein) are added.

In this work, we choose to study $V_2H$ at the $\beta_1\beta_2$-phase transition, which is from an ordered monoclinic atoms, both the $\beta_1$-phase to a disordered body-centered tetragonal (bct) $\beta_2$-phase in which the c-axis is along z (for the phase diagram, see [5]). While in the $\beta_1$-phase, mostly one sublattice, namely the z-axis octahedral $O_{Z1}$-sublattice, is occupied by hydrogen (H) atoms, both the $O_{Z2}$- and $O_{Z3}$-sublattices are occupied with equal probability in the $\beta_2$-phase [6]. The occupation of mainly $O_{Z2}$-sites in every other (0 k/2 k/2) plane leads to a periodic distortion of the vanadium (V) host lattice and thus to a (0 k/2 k/2) superstructure peaks (pseudo bct notation). The temperature-dependent measurement of superstructure peaks then allows us to extract the long-range order behavior.

Methods and Materials

We performed several x-ray diffraction experiments, both with high-energy x-rays in transmission geometry to probe the pure bulk and with low-energy x-rays in reflection geometry to measure the defective near-surface skin layer. The high-energy transmission x-ray experiment was done at the undulator beamline SRI-CAT, 1-ID beamline, at the Advanced Photon Source (APS) with an optimal x-ray energy of $E = 44.1$ keV from a Si-311 monochromator, together with a Si-111 analyzer crystal and a Geshid-state detector. We verified that there was no contamination from higher harmonics throughout the experiment. The reflection experiments were performed with Mo $K_{\alpha}$ x-rays at a RU-200 in-house rotating anode source, and with $E = 5.9$ keV and 9.0 keV x-rays at the beamline X14A at the National Synchrotron Light Source (NSLS). In the reflection experiments, we used a focusing Si-111 monochromator, and additionally for NSLS experiments, a Ge-111 analyzer crystal. We note that the effective penetration of the x-rays was tuned by choosing appropriate x-ray energies and incident angles which then yielded a depth sensitivity on a micron ($\mu$m) scale. The high-energy experiment in transmission and the low-energy experiments in reflection allowed us to detect separately the influence arising from a defective skin layer and from the bulk since we earlier observed two length scales in this crystal [1] (i.e., a broad “bulk” peak and a diverging sharp peak from the defective surface skin). In all experiments, the sample was mounted in a strain-free manner in vacuum of $\sim10^{-4}$ torr. The temperature fluctuations of the entire setup were less than 0.05 K at $T > 445$ K. Sufficient time, determined by quenching the sample and detecting the recovery of the superstructure reflection, was taken to reach equilibrium at each temperature.

Results and Discussion

Using x-rays in reflection geometry to tune the effective penetration of the probing x-rays, the long-range order parameter exponent in the defective skin layer can be determined from the integrated Bragg intensities, $I$, of superstructure reflections, where $I \propto \phi^\beta = -B(T/T_c - 1)^\beta$ and $\phi$ is the Bragg-Williams order parameter [7], $B$ a constant, and $\beta$ the critical exponent (for the data corrections see [8]). From the corrected integrated Bragg intensities of the (0 5/2 5/2) and (0 7/2 7/2) superstructure reflections, we obtained a value of $\beta = 0.13 \pm 0.02$ by including the narrow two-phase region (dashed line) as shown in Figure 1 a. Omitting the data point associated with the two-phase region (within 0.6 K) by treating, in this case, $T_c$ as a fit parameter as (e.g., in [9]) $\beta = 0.18 \pm 0.02$ is obtained (solid line), when both reflections were considered. If we neglect the influence of the two-phase region, our experimental value of $\beta$ indicates that we observe tricritical behavior in the defective skin layer although it is smaller than the theoretically expected value ($\beta = 0.25$). Our value is comparable with an earlier measurement [9] and with other tricritical systems (e.g., $\beta = 0.15$ in CsCoCl$_3$•2D$_2$O in [10], $\beta = 0.18$ in ND$_4$Cl in [11], and more recently [12] where $\beta = 0.16$ was obtained from lattice parameter data in ND$_4$Cl before applying lattice compressibility corrections, while $\beta = 0.22$ was found after the corrections).

On the other hand, the high-energy transmission experiment at the APS yielded a strong first-order phase transition in the bulk as shown in Figure 1 b), evidenced by a sharp drop of the (0 5/2 5/2) superstructure intensity by a factor of more than 400 at $T_c$. This is associated with a transition width of
~0.3 K, together with the abrupt broadening of the intensity profile at the superstructure position, shown in the inset of Fig. 1 b).

Figure 1: a) Corrected integrated intensities of the \((0 \, 5/2 \, 5/2)\) and \((0 \, 7/2 \, 7/2)\) superstructure reflections in a heating run versus \(\Delta T = T - T_C\), measured with MoK\(_\alpha\) x-rays to probe the defective near-surface skin layer. Neglecting the data point associated with a narrow (0.6 K) two-phase region and letting \(T_C\) vary as a fit parameter, we obtain \(\beta = 0.18 \pm 0.02\) (solid line) (for the two-phase region, see [8]). b) Peak height of the \((0 \, 5/2 \, 5/2)\) superstructure reflection versus \(\Delta T\) in a heating run, measured with high-energy x-rays in transmission to probe the (pure) bulk behavior which displays a strong first-order phase transition. Inset: FWHM of the \((0 \, 5/2 \, 5/2)\) bulk superstructure position versus \(\Delta T\).

In summary, we have observed a change in the order of the phase transition in a V\(_2\)H crystal, namely a discontinuous transition in the pure bulk and a continuous transition in the presence of defects in a near-surface skin layer. Since we earlier observed two length scales in this crystal [1], we have focused here on the separate influence of the pure bulk and the defective skin layer. We may exclude the possibility that the change in the order of the phase transition is due to a change of the position of the phase diagram between the defective skin layer and the pure bulk (evidenced by heat extraction and HERDA measurements), due to an oxygen gradient in the upper 150 Å, or due to phase separation and a crossing of a two-phase region within this sharp transition width of less than 0.3 K. We thus propose that the change in the order of the transition is due to the presence of random bonds or random fields, most likely prompted by the change in the mosaic spread within the defective skin layer (for a detailed discussion see [13]).

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References