Long-range order in V_2H near the β - ϵ phase transition

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The integrated intensity I of $h/20\bar{h}/2$ superstructure reflections has been measured with x rays for a single crystal of V_2H . Just below the critical temperature T_c of the β - ϵ phase transition, I varies as $(1 - T/T_c)^{2\beta}$ with $\beta = 0.153 \pm 0.007$, increasing to $\beta = 0.17$ and 0.20 when referred to a rigid volume and c lattice parameter, respectively, through a lattice-expansion correction. By comparing heating and cooling runs the second-order character of this phase transition has been demonstrated. A shift of T_c , however, was observed when data were taken without first thermally cycling the crystal close to T_c .

INTRODUCTION

The existence of various ordered and disordered arrangements of hydrogen in transition metals like vanadium, tantalum, and niobium and their structural transitions has stimulated many investigations in the past (for reviews, see Schober and Wenzl¹ and Asano and Hirabayashi²). Owing to their pronounced isotopic differences, the V-H and V-D systems are of particular interest.

Around $n_H/n_V = 0.5$ the V-H phase diagram shows three phases above room temperature: β , ϵ , and α (α').³ In the low-temperature β phase the hydrogen preferentially occupies one set of octahedral sites with the unique axis in the z direction (e.g., O_{z1}), i.e., sites on every second ($h\ 0\ \bar{h}$) plane (Fig. 1). This leads to a modulation of the vanadium host lattice, which becomes monoclinic or pseudotetragonal: $c/a = 1.1$, $\beta = 91^\circ$ at room temperature.^{4,5} Thus, $h/20\bar{h}/2$ superlattice peaks (a bct indexing is used in the following) are seen. It seems, however,

FIG. 1. (010) plane of V_2H with $\circ, \bullet$ for vanadium and $\square, \blacksquare$ for hydrogen atoms; note the $h\ 0\ \bar{h}$ modulation of the vanadium lattice indicated by the dashed lines. Open symbols, atoms in plane; solid symbols, atoms half a lattice spacing, $a/2$, off this plane.

that the crystal structure depends on the growth condition, and a tetragonal symmetry of V_2H at room temperature has been reported for crystals grown under an elastic stress.⁶ Upon heating the β phase into the ϵ phase the hydrogen becomes equally distributed on both O_z sites (O_{z1} and O_{z2}) and the superlattice peaks disappear. Recently, Watanabe and Fukai⁷ concluded from calorimetric studies that the O_{z1} and O_{z2} occupation is not a statistical one and a neighboring occupation of O_{z1} and O_{z2} sites is avoided, whenever possible; i.e., there is short-range order above the critical (β - ϵ) transition temperature. In addition, tetrahedral sites also seem possible.⁸ In the α (α') phase a disordered bcc solution is found with the hydrogen on random tetrahedral sites.

Controversies have arisen concerning the thermodynamic order of the β - ϵ phase transition. In early calorimetric and metallographic investigations Schober and Carl⁹ suggested a first-order character. Later, transmission-electron-microscope investigations³ led to a modification to second order, a result that was also suggested from electrical-resistivity measurements.¹⁰ To incorporate this second-order nature of the β - ϵ phase transition without violating basic phase-diagram rules, Moss¹¹ suggested a tricritical point close to $n_H/n_V = 0.5$.

THEORY

An order-disorder phase transition can be characterized by a set of critical exponents. These critical exponents are defined so as to describe the asymptotic temperature dependence, close to the transition temperature, T_c , of structural parameters such as the long-range order or the inverse correlation length (see, e.g., Stanley¹²). In the following the description and nomenclature have been adjusted to the case of the β - ϵ phase transition.

Below the critical temperature, T_c , the long-range or-

der is specified by the Bragg-Williams parameter

$$S = r_{O_{z1}} - w_{O_{z2}},$$

where $r_{O_{z1}}$ is the fractional hydrogen occupation on "correct" O_{z1} sites, while $w_{O_{z2}}$ gives a similar occupation on "incorrect" O_{z2} sites. There is, however, the additional possibility p_T for the hydrogen to occupy tetrahedral sites, thus leading to the normalization of $r_{O_{z1}} + w_{O_{z2}} + p_T = 1$. Because the exact ratio between the occupied octahedral and tetrahedral sites is unknown, an absolute determination of S is impossible. If one assumes a negligible fraction of tetrahedral sites ($p_T \ll S$) within the temperature range considered (see the schematic occupation probabilities of Hirabayashi⁸), the variation of S with temperature T can be determined,

$$S \sim (1 - T/T_c)^\beta,$$

with $1 - T/T_c \ll 1$. The integrated intensity I of a superstructure reflection is proportional to S^2 (see, e.g., Warren¹³) and thus allows us to determine T_c and β .

Above the critical temperature, T_c , $S = 0$ and only short-range order is present. This short-range order may be characterized by the Ornstein-Zernike pair-correlation function $p(r)$,

$$p(r) \sim r^{-1} \exp(-\kappa r),$$

where κ is the inverse correlation length and r the distance considered. This implies for the critical scattering intensity I_c ,

$$I_c(q) \sim (q^2 + \kappa^2)^{-1},$$

with q given by the distance from the superstructure reflection.¹² The asymptotic temperature dependence ($T/T_c - 1 \ll 1$) is given by

$$\kappa \sim (T/T_c - 1)^\nu.$$

Deviations from the above-mentioned form of $I_c(q)$ are expected for anisotropic systems, leading to an anisotropic inverse correlation length. Also, its Lorentzian shape may need corrections.¹⁴

EXPERIMENT

The vanadium single crystal, previously loaded with hydrogen by D. G. Westlake,¹⁵ had a n_H/n_V ratio of 0.50. The slice used in the present experiment was cut with a diamond saw to a thickness of 2 mm with a $[10\bar{1}]$ surface normal. This slice, of 0.5 in. diameter, was then mechanically polished. It showed three large areas of parallel stripe patterns with different stripe orientations. Such a multidomain martensitic appearance reflects the lowering of crystal symmetry upon cooling through the first-order ϵ - α transition.

Measurements were performed with a sealed x-ray tube [e^- impact (EI)] and also at a synchrotron-radiation (SR) source. In the EI setup, a Mo fine-focus x-ray tube operated at 35 kV and a Ge[111] monochromator of the Johann type were employed. Thus, Mo $K\alpha_1$, a symmetrical line profile with no contribution by

harmonics, was obtained. The SR measurements were done at HASYLAB, DESY, using the diffractometer on the D4.1 beamline in a double-axis configuration. With DORIS operating at 5–5.3 GeV, the flux of the chosen wavelength of 0.787 Å and its first few harmonics are of comparable order. To suppress the harmonics, we mounted a Au-coated mirror in addition to a flat Ge[111] monochromator. NaI scintillation counters were used and the incoming beam intensity was monitored by the scattered radiation from a Mylar foil (EI) and using an ionization chamber (SR), respectively.

The sample was heated in evacuated furnaces to reduce an increase of its protective oxide layer; the furnace used at HASYLAB has been described by Buras *et al.*¹⁶ The temperature T was controlled and determined by Chromel-Alumel thermocouples. With both furnaces the stability for a single scan used to determine the integrated intensity was better than ± 0.04 K. Because noncalibrated thermocouples were used with different mountings, the measurements yielded different values of the critical temperature T_c . Thus, a comparison of T_c values is only meaningful for a fixed setup.

RESULTS

Measurements were done at the superstructure reflections $1.50\bar{1}.5$ and $2.50\bar{2}.5$, about 30 min after reaching the measuring temperature T . Integrated intensities were obtained by ω scans, with a stepwidth of 0.1° in the wings of the reflections and 0.01° otherwise, and with an open counter technique. Repeating scans at a fixed temperature gave variations of typically less than $\pm 1\%$ in the integrated intensity, independent of the counting statistics and slightly increasing close to T_c . Owing to the high collimation of synchrotron radiation and sample inhomogeneity, variation of the sample spot illuminated (typically $1\text{--}2\text{ mm}^2$ to minimize temperature gradients), caused by variations of the e^- -bunch trajectory, had an observable impact on intensity. Thus, special care was taken to work in the center of a homogeneously scattering sample area.

Integrated intensities were obtained in heating and cooling runs. In comparison with a heating run, a shift of T_c by -0.6 K was observed in the cooling run. This difference was reduced to less than 0.2 K when several heating and cooling cycles (within $T_c + 5$ K and -10 K) preceded the measurement. As an example, Fig. 2 shows the results for the $2.50\bar{2}.5$ superstructure reflection. While increasing temperature, we observe a sharp decrease in the integrated intensity just below T_c , followed by distinct critical scattering above T_c . Simultaneously the full width at half maximum (FWHM) of this reflection decreases below T_c and sharply increases above T_c . Thus below T_c , the change from the monoclinic to the tetragonal crystal structure, which seems to show up in a decreasing FWHM, is more important for the FWHM than is its increase due to critical scattering. About the same percentage decrease in the FWHM close to T_c was observed in another SR run with a smaller incoming beam cross section, indicating the intrinsic character of this effect.

FIG. 2. Uncorrected integrated intensity ($\circ$) and FWHM of the ω scan (+) for the $2.50\bar{2}.5$ superstructure reflection (not unfolded).

To determine the critical exponent β , the integrated intensities have to be corrected for background, extinction, thermal vibrations, and critical scattering. A constant background was subtracted by using the intensity data at $\pm 2^\circ$ – 3° off the exact Bragg setting ω_{Br} . Whereas it amounted to less than 1 count/s with EI, it was 4 counts/s with SR. No temperature variation for extinction was applied to the integrated intensities, an approximation that can be tested by comparing the β value with different superstructure reflections.

Thermal diffuse scattering is not completely subtracted by using a straight background line, because it peaks beneath the Bragg reflection. Assuming its contribution to be small, it may be included in the effective Debye-Waller factor (DWF). For the $30\bar{3}$ fundamental reflection within $T_c - 10$ K and T_c , a 1.5% intensity reduction was found.¹⁵ Thus within the same temperature range, we expect 0.4% and 1.0% reductions, for the $1.50\bar{1}.5$ and $2.50\bar{2}.5$ superstructure reflections, respectively. It is well known that for alloys the Debye-Waller factor cannot be factorized out of the structure factor, and thus the effective DWF as determined from fundamental reflections will not, in general, be transferable to superstructure reflections. Owing to the large difference in the atomic scattering factors of vanadium and hydrogen, the effective DWF of the reflections under consideration is only determined by the DWF of vanadium at room temperature (to better than 1%).⁶ Thus, its use with superstructure reflections close to T_c seems to be plausible.

The measurements done below the critical temperature T_c also contain a contribution from critical scattering. To remove it, ω scans were also done above T_c with the same scattering geometry. These curves were then unfolded, basing the resolution function on three orthogonal scans through the superstructure peak (for details, see Als-Nielsen and Dietrich¹⁷) done at a temperature much lower than T_c where critical scattering is negli-

ble. A fitting of the unfolded ω scans then yields $\kappa_{T > T_c}$ and the proportionality factor. Adapting $\kappa_{T < T_c} / \kappa_{T > T_c} = \sqrt{5.2}$ with a temperature dependence $\kappa_{T < T_c} \sim (1 - T/T_c)^\nu$, $\nu \approx 1.0$ as determined above the critical temperature^{18,19} and the same proportionality factor, the critical scattering was calculated below T_c . In our measurements it amounted to as much as 10% close to T_c . This procedure is tentative, because it does not incorporate two features: (i) the resolution function that includes the mosaicity of the crystal—in addition to the instrumental resolution—changes close to T_c , as seen in the decreasing FWHM of the ω scan (Fig. 2), and (ii) an isotropic inverse correlation length is taken, due to the unknown scaling of the anisotropic correlation length above and below T_c , whereas a temperature-dependent anisotropy of the critical scattering is observed above T_c .

T_c and β were determined in a weighted least-squares fit of the corrected integrated intensities I to $I \sim (1 - T/T_c)^{2\beta}$. The weight w in the fit²⁰ was

$$w = \left[(\delta I)^2 + (\delta T)^2 \left(\frac{2\beta I}{T_c - T} \right)^2 \right]^{-1}$$

with the experimentally observed $(\delta I)/I = 0.01$ and $\delta T = 0.04$ K. The results are shown in Fig. 3 and the data are summarized in Table I.

Two items are noteworthy in Table I. First, the different reflections of run 1 agree well in β and T_c , as expected with proper corrections (including their neglect in the case of extinction). Second, whereas the EI measurements were done without cycling the temperature of

FIG. 3. Integrated intensity of run 1, (a) $1.50\bar{1}.5$ and (b) $2.50\bar{2}.5$; (c) run 2; and run 3, (d) cooling and (e) heating. The straight lines refer to data ($\square$) given without correction for a rigid volume, the dashed to data after this correction.

TABLE I. Critical exponent β of V₂H without and with consideration of a rigid lattice.

Run	Reflection			Not considering a rigid lattice		Considering a rigid: volume c parameter			Remarks
				T_c (K)	β	T_c (K)	β	β	
1	1.5	0	$\overline{1.5}$	443.25	0.156	443.15	0.169		EI
	2.5	0	$\overline{2.5}$	443.25	0.152	443.20	0.165		EI
2	2.5	0	$\overline{2.5}$	442.05	0.158	442.00	0.173	0.215	EI
3	2.5	0	$\overline{2.5}$	443.20	0.141	443.10	0.154	0.190	SR, heating
	2.5	0	$\overline{2.5}$	443.05	0.158	443.15	0.181	0.207	SR, cooling
				$\langle\beta\rangle=0.153\pm0.007$		$\langle\beta\rangle=0.168\pm0.010$		$\langle\beta\rangle=0.204$	

the sample close to T_c several times and without a pure heating run (but always staying below T_c), the SR measurements were performed after thermal cyclings, and pure heating and cooling runs were possible. With run 3 a larger variation in β is observed. This variation in β , however, is of the same order of magnitude as the scattering of data one obtains by deliberately omitting integrated intensities measured at temperatures closest or farthest away from T_c and thus not necessarily real.

To compare the experimental value of β with theoretical predictions, the data must be transferred to the case of a rigid lattice. This is achieved by a procedure similar to that used by Rechlin *et al.*²¹ First, the temperature variation of the lattice parameters a and c is taken from Jo *et al.*¹⁵ and Asano *et al.*²² After averaging, these data consistently describe the observed decrease of the $h0\bar{h}$ interplanar spacing $d_{h0\bar{h}}$ with increasing temperature. Second, from the pressure dependence of the critical temperature T_c and of the lattice parameters a and c (Ref. 23), one obtains $d \ln T_c / dp = 2.03 \times 10^{-2}$ GPa⁻¹ and $d \ln V / dp = -6.28 \times 10^{-3}$ GPa⁻¹, and the combination $d \ln T_c / d \ln V = -3.23$. The variation of T_c with the measuring temperature T is thus

$$T_c = T_c^0 \left[1 - 3.23 \frac{V(T) - V(T_c^0)}{V(T_c^0)} \right].$$

Because the lattice seems to be further away from the critical temperature (T_c^0) than in reality when referring to a rigid unit cell, a larger critical exponent β is obtained (see Table I). The increase in β to $\beta = 0.168 \pm 0.010$, however, is not large, because with increasing temperature T the lattice parameters a and c increase and decrease, respectively, in such a way as to reduce the value of $d \ln V / dp$.

Owing to the highly anisotropic character of the $h0\bar{h}$ modulation, one might alternatively correct for a rigid c lattice parameter, along the interacting distortion dipole axis, instead of a rigid volume. In this case there is no longer a partial cancellation of the lattice-parameter changes and larger corrections are expected for β . This evaluation, however, is problematic due to experimental uncertainties: the lattice parameters of Asano *et al.*²² and Jo *et al.*¹⁵ agree well in the a parameter, but are different in the c parameter, with the former data being larger. If one combines the latter data with the results of Fukai *et al.*,²³ one obtains $d \ln T_c / dp \approx 0$ GPa⁻¹ and

$d \ln T_c / d \ln c \rightarrow \infty$, and no conclusions are possible. On the other hand, a combination with the data of Asano *et al.*²² yields

$$T_c \approx T_c^0 \left[1 + 32 \frac{c(T) - c(T_c^0)}{c(T_c^0)} \right].$$

Correcting the data accordingly, straight lines as in Fig. 3 are, however, no longer observed within $1 - T/T_c < 2 \times 10^{-2}$. Sufficient data are only available with runs 2 and 3, yielding $\beta = 0.20$ (Fig. 4). Run 1 indicates a consistent value of β . For $1 - T/T_c > 4 \times 10^{-3}$ a slope of 0.24–0.28 is obtained. No decision can be made as to whether the finding with this tentative correction is only due to the uncertainties in $c(T)$.

Up to now, a negligible fraction of hydrogen on tetrahedral sites was assumed. If this is no longer valid, the Bragg-Williams parameter will only vary within 0 and $1 - p_T$ and corrections have to be made in order to compare the outcome for β with theoretical values ($p_T = 0$). No detailed data on p_T , however, are known close to the critical temperature T_c . In order to illustrate this influence, it may be assumed that p_T increases linearly from 0 at $T_c - 10$ K to a hypothetical value of

FIG. 4. Integrated intensity of (a) run 2, and run 3, (b) cooling and (c) heating with correction for a rigid lattice parameter c .

$p_T=0.03$ at T_c . Applying now a least-squares fit to $S=S(p_T)+p_T$, the critical temperature T_c will not vary by more than 0.05 K. The critical exponent β , however, will be reduced by ~ 0.021 . Naturally, a larger decrease of β will be found with a larger value of p_T .

DISCUSSION

The β - ϵ phase transition has been previously believed to be of second order. This was concluded from the smooth variation of the lattice parameters a and c close to T_c .²² Early measurements of superlattice reflections²⁴ also seemed to support this characterization. In addition, electrical-resistivity measurements¹⁰ showed no detectable hysteresis. With the present measurement we have shown that a hysteresis—if present at all—is less than -0.2 K. Thus, the second-order character of the phase transition seems rather plausible.

The reason for the hysteresis found in samples not thermally cycled before taking data is not yet understood. However, it is well known that the state of hydrogen in vanadium is very sensitive to stress (external and internal) and it might have been modified by cycling close to T_c . For example, a similar effect has been observed in the case of α -VH_{0.1} with channeling experiments,²⁵ suggesting that the site occupancy of hydrogen changes from tetrahedral T to $4T$ due to thermal cycling.

From electrical-resistivity measurements Bambakidis and Tober²⁶ deduced a critical exponent β of 0.35. Because the range of $1-T/T_c$, 3×10^{-2} to 9×10^{-3} , was far from T_c and only three data points were available, this value seems not to be conclusive. Whereas a value of $\beta=0.35$ would be rather close to that of a three-

dimensional Ising model ($\beta=0.31$), the present data ($\beta=0.17$ for a rigid volume and ~ 0.20 for a rigid c lattice parameter) resemble neither three-dimensional nor two-dimensional ($\beta=0.125$) Ising-model behavior.

Critical phenomena in highly anisotropic antiferromagnets (metamagnetic transitions; for a review, see Strykowski and Giordano²⁷) and the tricritical phenomena associated with them have been the subject of a number of investigations. A comparison with these findings seems attractive due to the assumed nearby tricritical point in V₂H. In contrast to the three-dimensional Ising model, a value of $\beta=0.25$ is predicted at the tricritical point. Neutron diffraction close to the tricritical point in CsCoCl₃·2D₂O by Bongaarts and de Jonge²⁸ yielded a different value of $\beta=0.15$ at the tricritical point and $\beta=0.28$ further off this point. Thus, this class of critical phenomena may be a more appropriate description of the long-range order in V₂H close to the β - ϵ phase transition. In V₂H the anisotropic (axial) elastic dipolar interaction between interstitial H atoms may be seen to stand for the anisotropic magnetic interaction in the metamagnets.

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