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X-RAY STUDY OF THE PRECIPITATION OF HYDROGEN IN VANADIUM*

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Many anomalies have been reported for the behavior of vanadium at low temperature.[1] In particular, Colella, Batterman and Kashyap[2] during the study of the x-ray diffuse scattering in vanadium single crystals have observed an extra scattering at low temperature in certain regions of reciprocal space.

Westlake[1,3,4] pointed out that vanadium getters considerable amounts of hydrogen in very common laboratory operations such as mechanical, chemical, and electrochemical polishing. Then, supposedly "pure" vanadium can actually be a vanadium-hydrogen alloy. On this basis most of the reported anomalies can be explained in terms of the precipitation of second phase which is predicted from the equilibrium diagram for the vanadium-hydrogen system. Taking into account Westlake's results, Colella, Batterman and Kashyap attributed the low temperature extra

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scattering to hydrogen impurities. This was borne out experimentally since the extra scattering disappeared after the crystals were given the particular vacuum anneal which is known to remove dissolved hydrogen.

The aim of this note is to report further evidence about the structure effects of hydrogen impurities in vanadium single crystals. We used for our experiments one of the unannealed single crystals used in previous studies by Colella, Batterman and Kashyap.[2] The crystal was cut on the (100) planes, mechanically polished by conventional metallographic techniques and finally chemically polished in a 1:1 HNO_3:HF mixture. The chemical analysis by emission spectrography has shown the following metallic impurities: silicon and iron less than 50 ppm; manganese and copper less than 10 ppm (concentrations in ppm by weight).

Two X-ray techniques were used:

1. Counter goniometer technique with CuKα monochromatic radiation obtained with a doubly bent LiF crystal. A proportional counter with pulse high selector was used to suppress the $\lambda/2$ harmonic and most of the vanadium fluorescence, which was further attenuated by aluminum foils.

2. Berg-Barrett photographic techniques with filtered CuKα radiation, with the film normal to the diffracted beam.

In both cases the vanadium crystal is mounted in a cryostat already described by Batterman and Barrett.[5] The temperature, which can be varied in a wide range, is measured with a platinum resistance thermometer.

Fig. 1 shows the results obtained in two runs with the counter goniometer in which the intensity distribution along the [100] axis of the reciprocal lattice was determined at 90°K and at 300°K. At 300°K only the vanadium (200) peak is observed above the background. At 90°K, however, two supplemental peaks appear, one at 1.81 and the other at 3.60, in units of the vanadium reciprocal lattice. The intensity of the latter is about 1/10 of the former's. These peaks are consistent with the body centered tetragonal vanadium hydride (002) and (004) reflections, predicted from the lattice parameters given by Maeland[6] ($a = 3.002 \mathring{A}$, $c = 3.302 \mathring{A}$).

We interpreted the two observed extra peaks as due to the tetragonal vanadium hydride which precipitates at low temperature.

With asymmetric runs we explored arcs across the [100] axis in reciprocal space to determine the intensity distribution across this axis. We determined in this way that the (002) and (004) peaks were centered on the [100] axis of the vanadium reciprocal lattice. This fact allows us to conclude that the precipitation of the bct hydride occurs coherently with its {001} planes parallel to the {100} planes of the vanadium matrix.

The integrated intensity of the (002) hydride peak was determined as a function of the temperature. This was accomplished by beginning at low temperature and, then, heating the specimen at various temperatures. At each temperature we allowed about half an hour before measuring the intensity. The results are shown in Fig. 2. When temperature rises from 220°K the integrated intensity drops and reaches the background at about 280°K. Measurements of the peak intensity made during the continuous cooling of the cryostat shows that the (002) intensity begins to rise at 278°K. Considering the existing data bout the solubility limit of hydrogen in vanadium,[7,8] if the precipitation begins at that temperature it means that the measured crystal acquired through normal handling and preparation, as much as 2 at. % of hydrogen. This value is not unusual in vanadium that has not been vacuum annealed.[1,3]

In Fig. 3 are shown two Berg-Barrett photographs obtained from the (200) vanadium reflection. The picture at 200°K shows clearly an oriented precipitate. In the picture at 300°K only the imperfections on the crystal surface are evident. The doubling of vertical features is due to the superposition of α_1-α_2 images. All perceptible trace of the precipitate on Berg-Barrett pictures seems to disappear at 273°K. At this temperature, however, the integrated intensity have still an appreciable value above the background.

Because of the exposure time to obtain a Berg-Barrett photograph, we could not see, with this technique, how and at what temperature precipitation effects become evident during the continuous cooling.

With modifications in the cryostat it was possible to make some optical metallographic observations with a magnification of about 50. These observations agree quite well with the x-ray results. At low temperature an oriented precipitate is observed (Fig. 4a) and no changes are detected between 90°K and 250°K. Thereafter, the precipitate platelets become thinner when temperature rises. Finally, observations between 265°K and 310°K during times as long as 30 hours show no changes on the crystal surface. It was concluded, then that the precipitate in that range was already dissolved, but they left marks or steps on the crystal surface (Fig. 4b). On cooling, the precipitate forms exactly on those marks at an extremely high rate. These facts make it rather difficult to determine the temperature at which precipitation starts. The precipitate is, however, evident, at temperatures lower than 265°K. As was pointed out above, at this temperature, the x-ray (002) intensity had already started to rise.

According to the sensitivity of the different observation methods used in the present work, we can split the precipitation and dissolution of vanadium hydride in two stages. In one stage the phenomenon is easily detected by the Berg-Barrett and low magnification metallographic methods. In the other stage, the only evidence of hydride precipitation is the weak (002) x-ray intensity. The separation between the stages is just a few °K. The most obvious idea is that the only difference between them is the scale in which changes occur but the phenomenon involved is the same. There is still the possibility of another stage, more subtle, whose effects would not be detected in our experiments.

Recently, Sherman, Owen and Scott[9] concluded from metallographic observations that the hydride precipitation occurs martensitically. This would require a local atomic rearrangement of the hydrogen before precipitation in order to reach the hydride composition. The authors suggested that the ductile-to-brittle transition observed in vanadium-hydrogen alloys might be associated with local ordering before precipitation. Actually, they observed the embrittlement transition at temperatures 15°K higher than that at which the hydride precipitation was detected.

The high diffusion rate of the hydrogen could make it particularly difficult to distinguish a martensitic from a diffusional process. Neutron diffraction techniques are difficult to apply in this case because of the high incoherent cross section of vanadium. However, there is evidence, under certain conditions,[10] that supports the hypothesis of the local ordering of hydrogen. Nevertheless, some of Sherman et al.'s results seem to be difficult to explain on this basis. Actually if ordering occurs 15°K before precipitation, it is quite reasonable to expect an appreciable affect on the electricl resistivity. However, the solubility curve of hydrogen in vanadium determined by Sherman et al. by metallographic observations agree very well with the solubility curve determined by Westlake from electrical resistivity measurements and these are both 15°K below the temperature at which embrittlement occurs.

If, instead of a martensitic process, a diffusional precipitation of the hydride is assumed, it is not necessary for there to be local ordering before precipitation since only a nucleation and precipitate growth process is involved. It is possible then that for a given hydrogen concentration and observation time, the temperature at which the size and distribution of nuclei are such that the electrical resistivity is affected is quite close to the temperature at which precipitates can be detected metallographically. In our experiments, we observe extra diffuse (002) intensity just a few degrees above the range where the precipitate is visible metallographically. In other words, our x-ray scattering results are not inconsistent with the hypothesis that the precipitation is the final stage of a nucleation and growth process. We cannot, at this stage of our work offer any concrete explanation for the fact that the embrittlement occurs at a temperature 15°K higher than that at which precipitation is detected.

ACKNOWLEDGMENTS

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FIGURE CAPTIONS

Figure 1 - Intensity distribution in the [100] direction of the vanadium reciprocal lattice at 300°K and 90°K. Arrows indicate the body centered tetragonal vanadium hydride (002) and (004) reflections, predicted from the lattice parameters given by Maeland.[6]

Figure 2 - Variation of the (002) vanadium hydride integrated intensity as a function of temperature.

Figure 3 - Berg-Barrett photographs obtained from the (200) vanadium reflection. The doubling of vertical features is due to the superposition of α_1-α_2 images.

Figure 4 - Optical metallography of the vanadium crystal (100) surface: (a) at 200°K, (b) at 300°K.

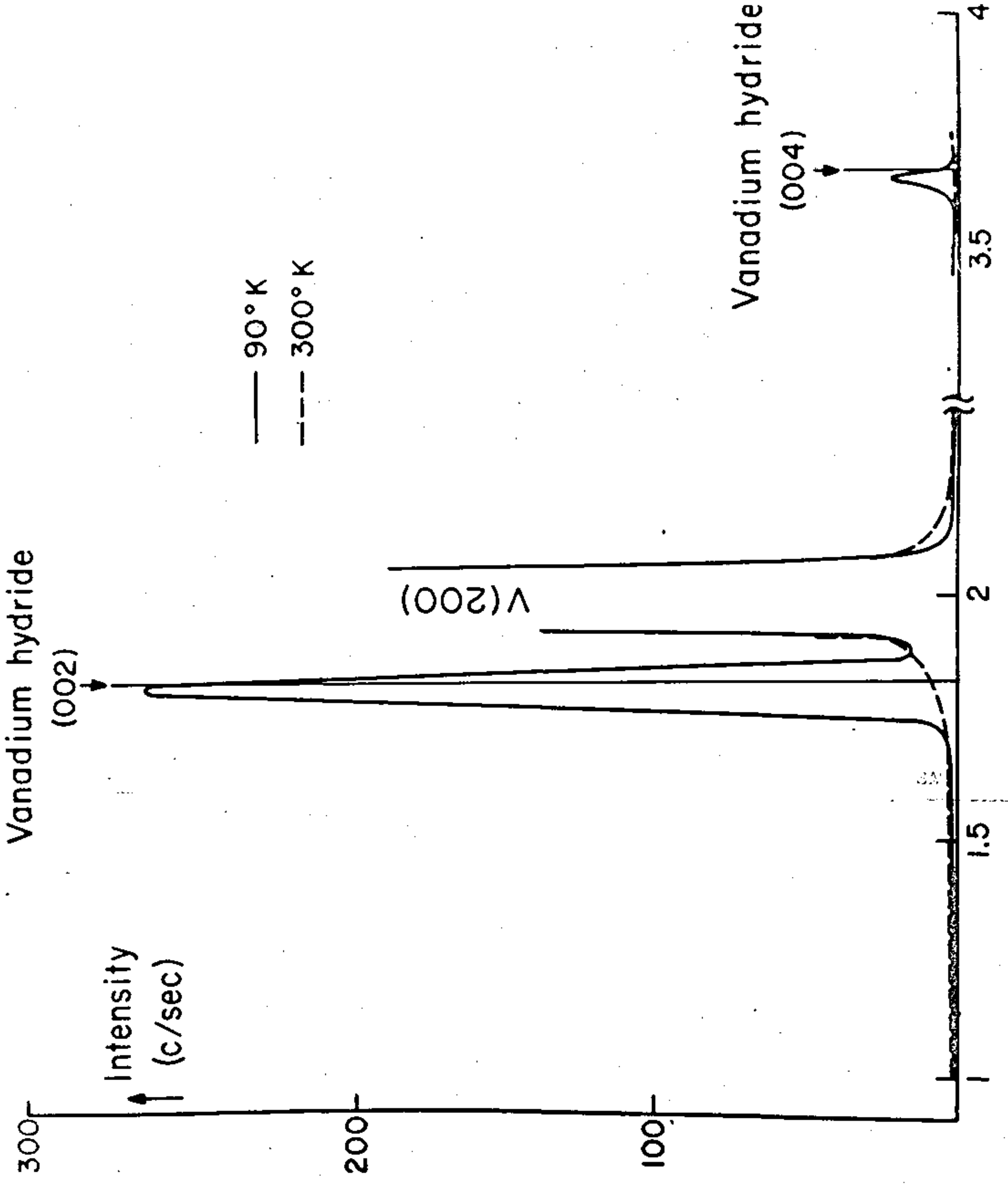

Intensity (c/sec)
300
200
100
1
1.5
2
3.5
4
hoo →
Vanadium hydride (002)
V(200)
Vanadium hydride (004)
90° K
300° K

Figure 1

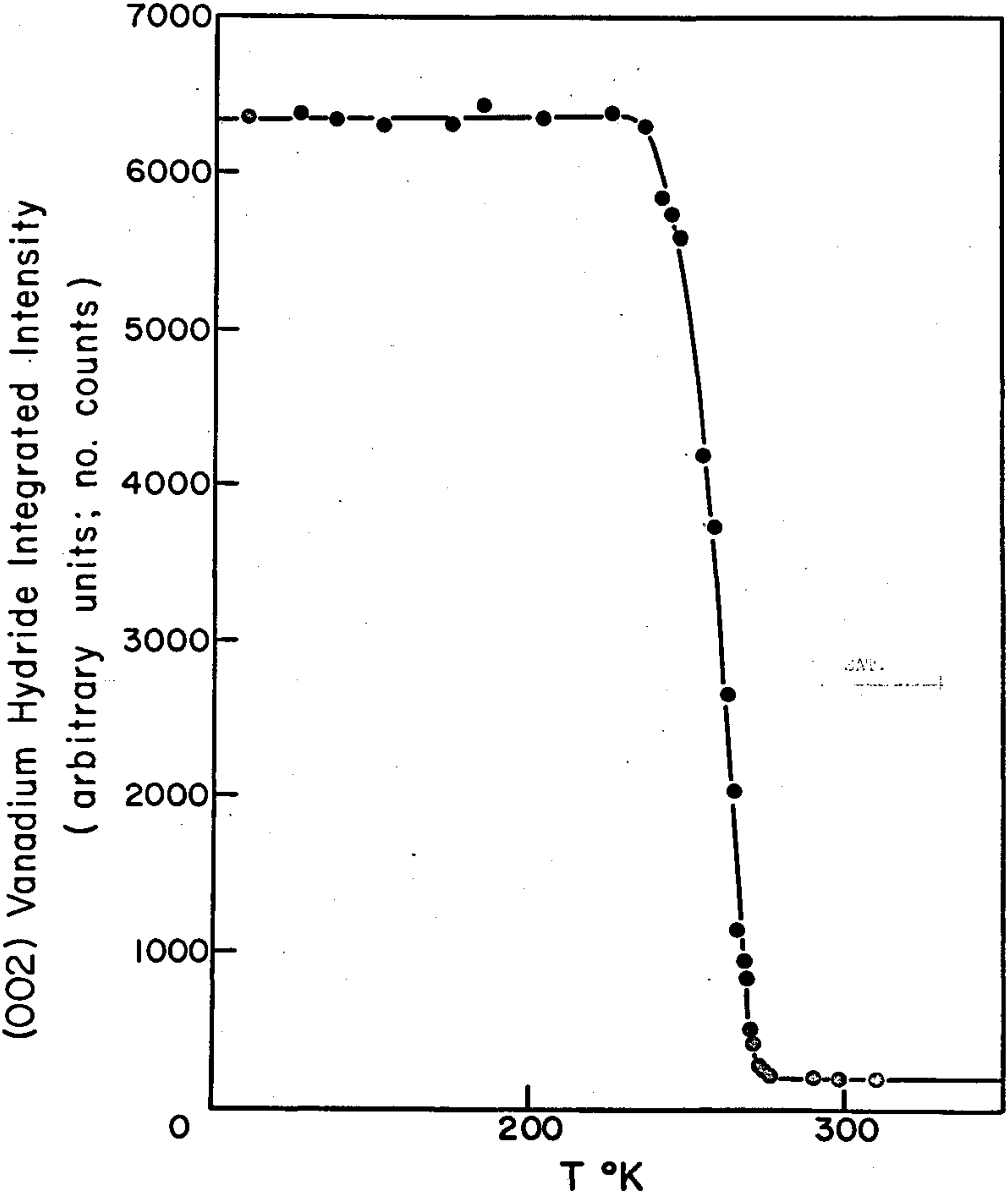
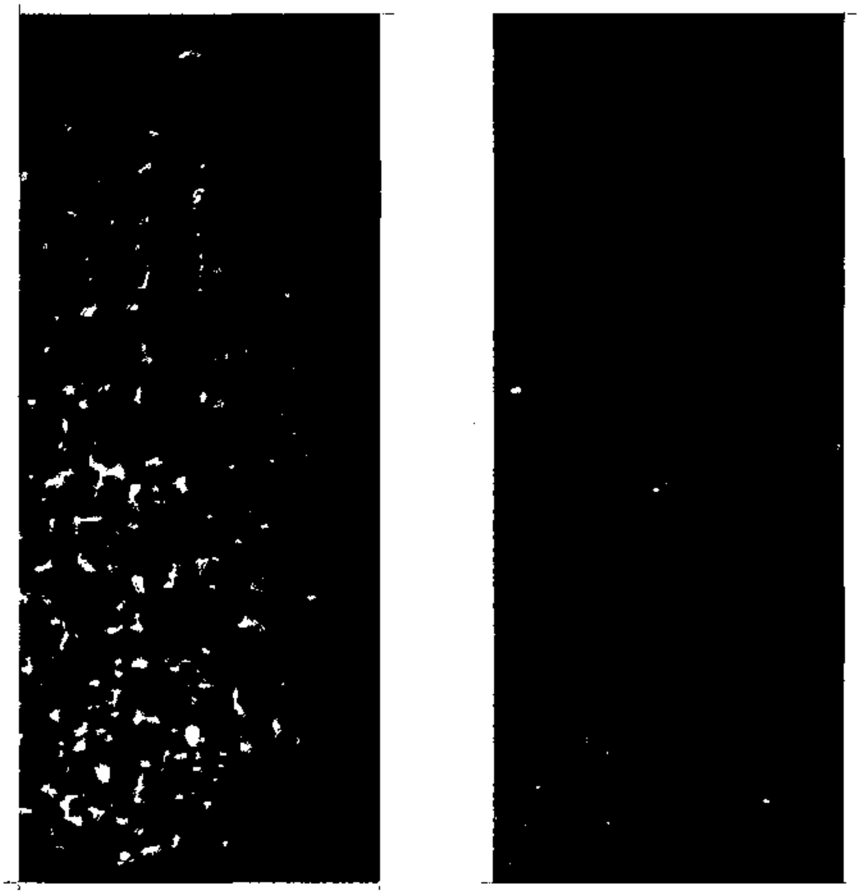
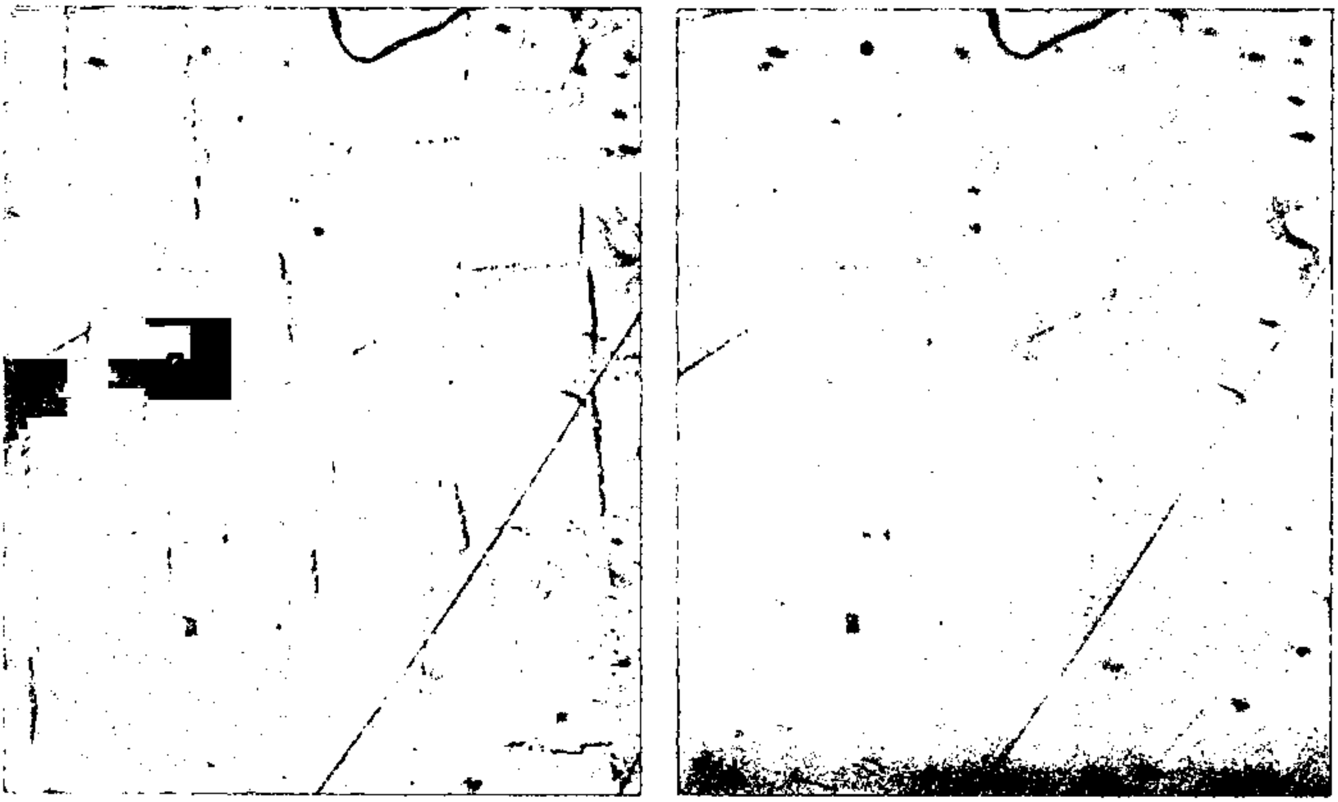

7000
6000
5000
4000
3000
2000
1000
0
200
300
T °K
(002) Vanadium Hydride Integrated Intensity
(arbitrary units; no. counts)

Figure 2



200°K 300°K

Figure 3.



200°K

300°K

Figure 4.