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High-pressure/temperature structural phase transition in vanadium: Influence of non-hydrostatic conditions

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Vanadium has been reported to undergo phase transition upon compression from bcc to rhombohedral structure around 62 GPa. In this paper we confirm the bcc to rhombohedral phase transition at 61.5 GPa under quasi hydrostatic compression in Ne pressure medium. Under non-hydrostatic condition we find the phase transition occurring at 30 GPa at ambient temperature, and 37 GPa at 425 K. We find the transition under hydrostatic condition is hindered and it can occur at much lower pressure under non-hydrostatic condition.

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I. INTRODUCTION

Vanadium is a transition metal that has been subject of recent theoretical and experimental studies. Early theoretical studies of the structural phase stability, based on simple model predicted most of the trends in the transition metals regarding their structure under ambient and high pressure conditions.[1] The prediction of a very stable body-centered cubic (bcc) structure for group 5 transition metals was confirmed in the case of Ta, up to ~200GPa.[2] However, in case of the vanadium this prediction of a very stable bcc structure is not consistent with experimental results and modern theoretical calculations.

In a theoretical study of the superconducting transition temperature behavior under high-pressure conditions, Suzuki and Otani performed first-principles calculations of the lattice dynamics of vanadium in the pressure range of up to 150GPa.[3] They found that the transverse acoustic phonon mode TA [ξ00] around $\xi=1/4$ shows a dramatic softening under pressure and becomes imaginary above 130 GPa, indicating the possibility of a structural phase transition. Later, Landa *et al*. performed total energy calculations for the trigonal shear elastic constant (C_{44}) of vanadium in the bcc phase.[4] Their results identified a mechanical instability in C_{44} around 200 GPa, preceded by a change in the slope of its pressure-dependence beginning at ~60GPa. The authors attribute the instability in the trigonal shear elastic constant to an intra-band nesting feature of the Fermi surface.

Later Ding *et al.* performed experimental studies, confirming that indeed vanadium undergoes a pressure-induced phase transition from the bcc to a rhombohedral structure at 69GPa.[5] Further first-principles calculations confirmed the experimental identified rhombohedral phase in vanadium.[6,7] Furthermore, Lee *et al.* found two different rhombohedral phases in their studies β, γ phases that differ from each other only in the angle between the rhombohedral basis vectors. The stability range of these two rhombohedral phases are followed by a transition back to the bcc structure above 280 GPa pressure, which is predicted to remain the energetically stable structure up to at least 400 GPa according to Luo *et* al.[8] The most recent theoretical study of vanadium phase stability indicates the transition to the first rhombohedral phase at 60 GPa and the transition to the high pressure bcc phase at 310 GPa.[9]

It is interesting to note that Ding *et al*. found that under non-hydrostatic conditions the phase transition from bcc to rhombohedral structure occurred at a higher pressure of 69 GPa, in contrast to the transition pressure of 63 GPa under quasi-hydrostatic conditions. These results are at odds with the typical expectation that non-hydrostatic conditions lower the transition pressure compared to hydrostatic and quasi-hydrostatic conditions.[10,11,12] This unusual behavior of the reported phase transition prompted our interest in further studies of the transition. In the following we present our findings using both non-hydrostatic and quasi-hydrostatic pressure transmitting media.

II. EXPERIMENT

For our high-pressure studies of vanadium, we used a membrane diamond-anvil cell (mDAC) with 0.2 mm flat and 0.1/0.3 mm beveled diamond anvils for moderate and high pressure ranges respectively. We used 0.25 mm thick Re gaskets, pre-indented to up to 25 GPa, corresponding to gasket thickness of 21-24 μm. Either a 120 μm (moderate pressure) and 60 μm (high pressure) hole was EDM drilled in the center of the indented area to form the sample chamber. The source for sample was Alfa Aesar's Vanadium powder, -325 mesh, with a purity of 99.5%. For quasi hydrostatic experiments small, 5-10 μm diameter vanadium grains were loaded together with small Pt particle for pressure marker. The pressure transmitting media (argon, neon, helium) was loaded in a 30000 psi high pressure gas loader at 0.165 GPa, initial pressure manually increased to 2-3 GPa with the screws in the loading chamber. For non-hydrostatic studies the sample chamber was packed with V powder and a few Pt particles (<2 μm size) were added to serve as a pressure marker. The choice for the pressure marker of Pt was motivated by two reasons: 1) it has minimal overlapping lines with the diffraction pattern of the sample, and 2) a well-calibrated high-pressure and temperature EOS. Even with these benefits, we were very careful to use in our analysis clean diffraction patterns, containing diffraction only from the sample. To heat the sample we chose a simple method of wrapping a commercial heating coil (Tempco Inc.) around the mDAC and insulating it from ambient heat-sinks using several layers of aluminum foil. This simple approach was possible since our target temperatures were less than 200 °C. Angle dispersive X-ray diffraction experiments were carried out at HPCAT at the Advanced Photon Source at Argonne National Laboratory, at Sector 16. Diffraction patterns were collected over the course of several different experimental runs using monochromatic x-ray beams of typically of 25 keV or 30 keV. The diffraction patterns were collected with a MAR345 image plate with typical exposure times varying between 30-120 s. The 2D images collected were integrated using Fit2D[13] to obtain an intensity curve of the diffraction peaks as a function of the 2θ angle, which were analyzed to obtain the cell parameters using the XRDA[14] and JADE software packages.

III. RESULTS AND DISCUSSION

Our initial study was carried out on a sample loaded without a pressure medium and compressed to pressures well beyond the phase transition pressure (>15 GPa). During the transition from the bcc to the rhombohedral structure, it can be seen in the integrated pattern that the bcc 110 and 211 peaks split into two and three peaks respectively. Initially the new rhombohedral peaks are very close to each other and cannot be resolved in the integrated 2θintensity plot. However, in the 2D image of the Debye-Scherrer rings, distinct lines could be seen at different positions. What is easily measurable on the integrated pattern is the width of individual diffraction peaks and a broadening of the above mentioned two peaks can be observed. These changes are easily identified, since the 200 peak from the bcc does not split through the transition, and remains very sharp. In Fig. 1 we present a few representative integrated 2θ-intensity diffraction patterns from the non-hydrostatic sample, the broadening of the 110 and 211 peaks is evident and used to identify the transition and becomes more pronounced with the increasing pressure. To within the experimental accuracy, we do not observe an abrupt splitting of the diffraction peaks, but instead a continuous and increasing separation. This, in the pressure range relevant to transition can be seen in Fig. 2 where we show the width of the 110 peak as a function of the pressure. At 82 GPa under non hydrostatic compression the split of the 110 bcc peak into the -110 and 100 rhombohedral peaks is clearly visible in the 2D diffraction image shown in Fig. 3. While the individual peaks of the split 211 bcc peak are not distinguishable, the strong broadening of the ring can be observed. Our experiments at room temperature for non-hydrostatic compression identify a transition pressure of 30 GPa which is much lower than previously reported by Ding *et al*. Our data shows unambiguously that the phase transition occurs at this lower pressure both from the peak broadening and the diffraction pattern hkl-indexing, which fits the rhombohedral structure very well. To confirm this lower transition pressure of 30 GPa and determine the temperature dependence, we performed non-hydrostatic compression experiments on several different samples at ambient and at higher temperature as well. Raising the sample temperature to 425 K yielded similar results: during compression of the sample from 20 GPa to 75 GPa we observe changes in the diffraction patterns entirely analogous to the room temperature experiment. The

110 and 211 bcc diffraction peaks broaden and split while the 200 peak remained as a single sharp peak confirming again the transition from cubic to rhombohedral phase. The only difference induced by the temperature is a shift of the transition pressure from 30 GPa to 37 (±2) GPa. This transition pressure is higher than the room temperature value, showing a positive slope for the cubic-rhombohedral vanadium phase boundary on the P-T diagram. The obtained rhombohedral phases for both the 300 K and 425 K samples are consistent with previous studies as expected. At the transition pressure of 30 GPa at room temperature we obtain a rhombohedral unit cell with cell parameter $a_R=2.51031(\pm 0.002)$ Ǻ with $\alpha=109.61(\pm 0.018)^o$, which is smaller than the theoretically expected 110.25°, but consistent with a second order transition suggested by previous experiments.[5] A fit of the diffraction pattern to rhombohedral phase using the JADE software package is shown in Fig. 4. We fit a Vinet-form universal equation of state (Ref.15) to our pressure-volume points for the rhombohedral phase and obtained the following fitting parameters: $K_0=202(\pm 37)$ GPa for the bulk modulus and $K_0'=1.71(\pm 1.51)$ for its derivative. These results, with the exception of the bulkmodulus derivative, are in good agreement with previous experimental results ($K_0=195$ GPa and $K_0'=3.5$ (ref.5).

We also performed quasi-hydrostatic experiments on vanadium samples using different pressure media: Ar, Ne and He. While Ar is a noble gas it is known that under pressure it stiffens with increasing pressure, becoming less hydrostatic medium than He or Ne.[16-21] As expected, we found that the phase transition pressure for vanadium samples in Ar is much closer to the previously reported 63GPa which used He as pressure medium. In our experiments when vanadium is compressed to 80 GPa in an Ar pressure medium, we found the transition pressure to be 53GPa. When we change the pressure medium to Ne, which is much softer than Ar at similar pressures, we observed a transition pressure of 61.5 GPa, which is very close to the transition pressure of 62 GPa reported by Luo et al. as a result of their lattice dynamics calculations and just 1 GPa lower than experimental data obtained by Ding et al. Fitting this data to a Vinet EOS we find that the vanadium pressure-volume data collected using the Ne pressure medium yields fitting parameters for the bulk modulus and its derivative of K_0=179(8) GPa and K_0'=3.11(1.23) respectively (see Fig. 5). These parameters are closer to Ding et al.'s quasi-hydrostatic parameters for bcc vanadium and are also in good agreement with the latest theoretical values of K_0=182 GPa and K_0'=3.75 published by L. Koči et al.[22] As anticipated, experiments performed on vanadium in a He pressure medium yield a transition pressure even higher than the case of the Ne, while the two P-V curves overlap. We found the transition pressure in He pressure medium to be 65 GPa, which one can assume to be the lower limit of the transition pressure in an ideal hydrostatic environment. Here we note that regardless of the pressure media used or in experiments without pressure media, to within our experimental errors we do not find a change in unit cell volume across the bcc-to-rhombohedral transition. The volume change calculated by Lee et. al for the first phase transition of 0.03% cannot be experimentally verified since it is within the margin of experimental error.[7] Based on the contention of Lee et al., that the bcc structure of vanadium is mechanically stable, though energetically/thermodynamically unfavorable, in the range where the rhombohedral phase is the ground state,[7] the transition from bcc-to-rhombohedral might not occur under all experimental circumstances, and the bcc phase may persist as a metastable phase. However, with increasing pressure the metastability may become less energetically stable. Further, non-hydrostatic conditions could provide the mechanical mechanism to overcome any energy barriers to the transition and drive the transition to the rhombohedral phase.

The reported high pressure rhombohedral phase of vanadium can be characterized as an elongation of the body diagonal of the primitive cell of the bcc unit cell. The strain induced in the sample by the pressure gradients due to non-hydrostatic compression seems to favor deformation along the 111 body diagonal at much lower pressures than in the ideal hydrostatic case. In the ideal situation of hydrostatic conditions at the transition, theoretical calculations reveal that both phases of vanadium are energetically very close to each other and separated by a low energy barrier that would make it a first order transition at zero temperature[6,7]. However, at higher temperatures, because the thermal fluctuations are expected to be larger than the latent heat of the transformation the true nature of the transition cannot be easily determined. Even if the energy barrier between the bcc and rhombohedral phases is small, it appears that the hydrostaticity of the compression medium has a directly influences the transition pressure. In the non-hydrostatic case, when the sample is compressed by the two diamond anvils and contained only by the stiff Re gasket the transition occurs at 30 GPa and as the strength of the pressure media decreases the transition pressure approaches to the hydrostatic condition transition pressure. So far there have been no theoretical studies on the influence of the hydrostatic conditions on the transition pressure in vanadium, but in case of other transition metals the scatter in the transition pressure has been explained by the shear stresses.[23]

IV. CONCLUSION:

Our experiments confirm the existence of previously reported rhombohedral phase of vanadium at high pressure. We report a dependence of the transition pressure as a function of the hydrostatic condition of the pressure media. Less hydrostatic conditions lead to a lower the transition pressure. We find the bcc→rhombohedral phase transition occurring as low as 30 GPa without any pressure medium and as high as 65 GPa. We propose that the true thermodynamic phase transition pressure should be associated with the 30 GPa value. Higher pressure transitions are the results metastability of the bcc phase due to energy barriers to the transformation. We also report a positive slope for the bcc→rhombohedral transition under non-hydrostatic conditions.

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REFERENCES

[1] J. A. Moriarty, Phys. Rev. B **45**, 2004 (1992).

[2] H. Cynn and C.-S. Yoo, Phys. Rev. B **59**, 8526 (1999).

[3] N. Suzuki and M. Otani, J. Phys: Condens. Matter **14,** 10869 (2002).

[4] A. Landa, J. Klepeis, P. Soderlind, I. Naumov, O. Velikokhatnyi, L. Vitos, and A. Ruban, J. Phys.: Condens. Matter **18**, 5079 (2006).

[5] Y. Ding, R. Ahuja, J. Shu, P. Chow, W. Luo, and H-K. Mao, Phys. Rev. Lett. **98**, 085502 (2007).

[6] B. Lee, R. E. Rudd, J. E. Klepeis, P. Söderlind, and A. Landa, Phys. Rev. B **75**, 180101(R), (2007).

[7] B. Lee, R. E. Rudd, J. E. Klepeis, and R. Becker, Phys. Rev. B **77**, 134105 (2008).

[8] W. Luo, R. Ahuja, Y. Ding, H.-K. Mao, PNAS **104**, 16428 (2007).

[9] A. Landa, O. Söderlind, A.V. Ruban, O.E. Peil, and L. Vitos. Phys. Rev. Lett. **103**, 235501 (2009).

[10] Y. Ma, E. Selvi, V. I. Levitas, and J. Hashemi, J. Phys.: Condens. Matter **18**, S1075–S1082 (2006).

[11] N. Von Barge and R. Boehler, High Pressure Research **6**, 133 (1990).

[12] D. Errandonea, Y. Meng, M. Somayazulu, and D. Hausermann, Physica B **355,** 116-125 (2005).

[13] A. P. Hammersley, S.O. Svensson, M. Hanfland, A.N. Fitch, D. Hausermann, High. Pres. Res. **14**, 235 (1996).

[14] K. Lagarec and S. Desgreniers, J. Appl. Crystallogr. **31**, 109 (1998).

[15] P. Vinet, J. Ferrante, J. Rose, and J. Smith, J. Geophys. Res. **92**, 9319 (1987).

[16] J. H. Burnett, H. M. Cheong, and W. Paul, Rev. Sci. Instrum **61**, 3904 (1990).

[17] K. Takemura, J. Appl. Phys, **89**, 662 (2001).

[18] H. Shimizu, H. Imaeda, T. Kume, and S. Sasaki, Phys. Rev. B **71**, 014108 (2005).

[19] D. Errandonea, R. Boehler, S. Japel, M. Mezouar, L.R. Benedetti, Phys. Rev. B **72**, 092106 (2006).

[20] A. Dewaele, F. Datchi, P. Loubeyre, and M. Mezouar, Phys. Rev. B **77**, 094106 (2008).

[21] S. Klotz, J-C. Chervin, O. Munsch, and G. Le Marshand, J. Phys. D: Appl. Phys. **42**, 075413 (2009).

[22] L. Koči, Y. Ma, A. R. Oganov, P. Souvatzis, and R. Ahuja, Phys. Rev. B **77**, 214101 (2008).

[23] K.J. Caspersen, A. Lew, M. Ortiz and E.A. Carter, Phys. Rev. Lett. **93**, 111501 (2004).

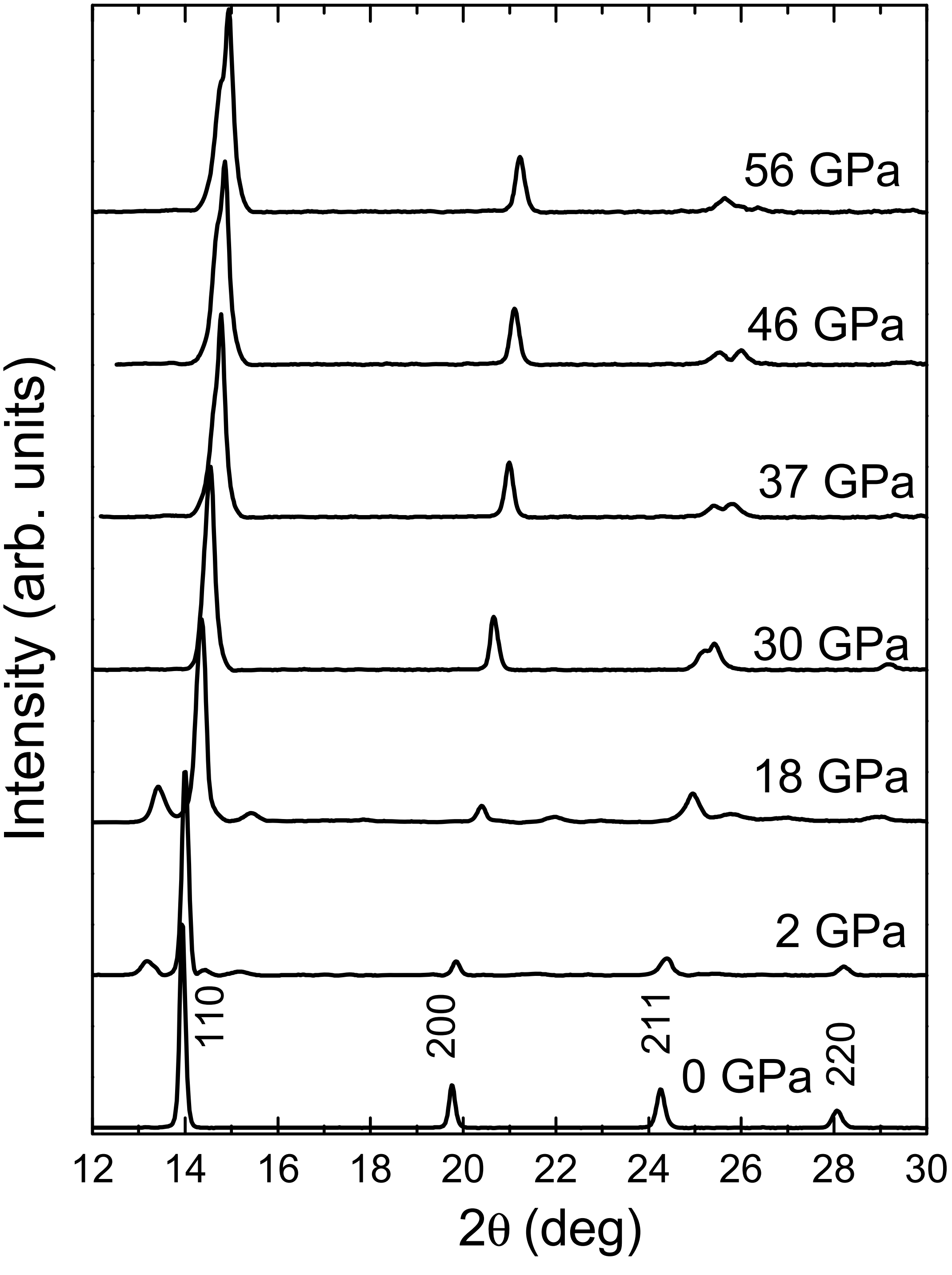

FIG. 1. Integrated XRD patterns of vanadium showing broadening of 110 and 211 peaks across the bcc-rhombohedral transition as compressed without pressure media under non-hydrostatic conditions. (λ=0.51822Å)

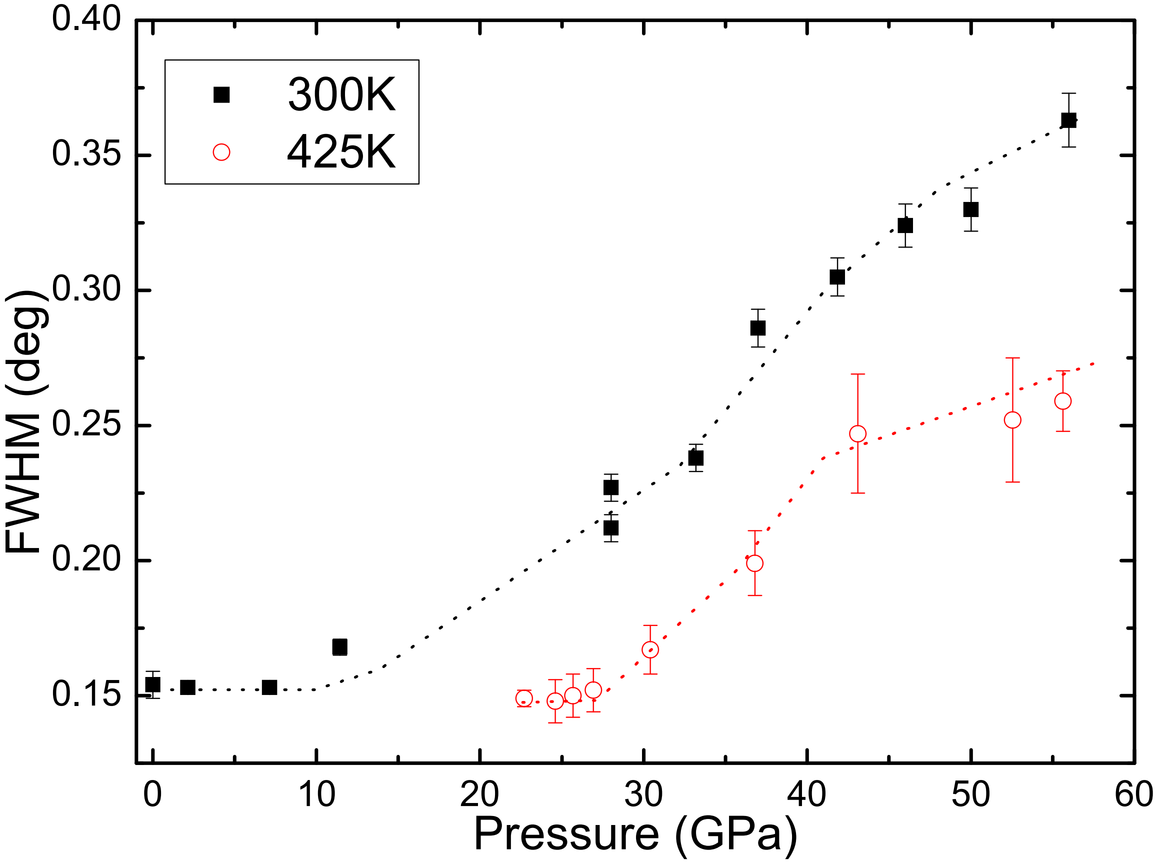

FIG. 2. (Color online) 110 diffraction peak full width at half maximum as a function of pressure as measured under non hydrostatic conditions. Full squares (black) at ambient temperature, empty circles (red) at 425 K; dotted lines manual fit, guide to the eye.

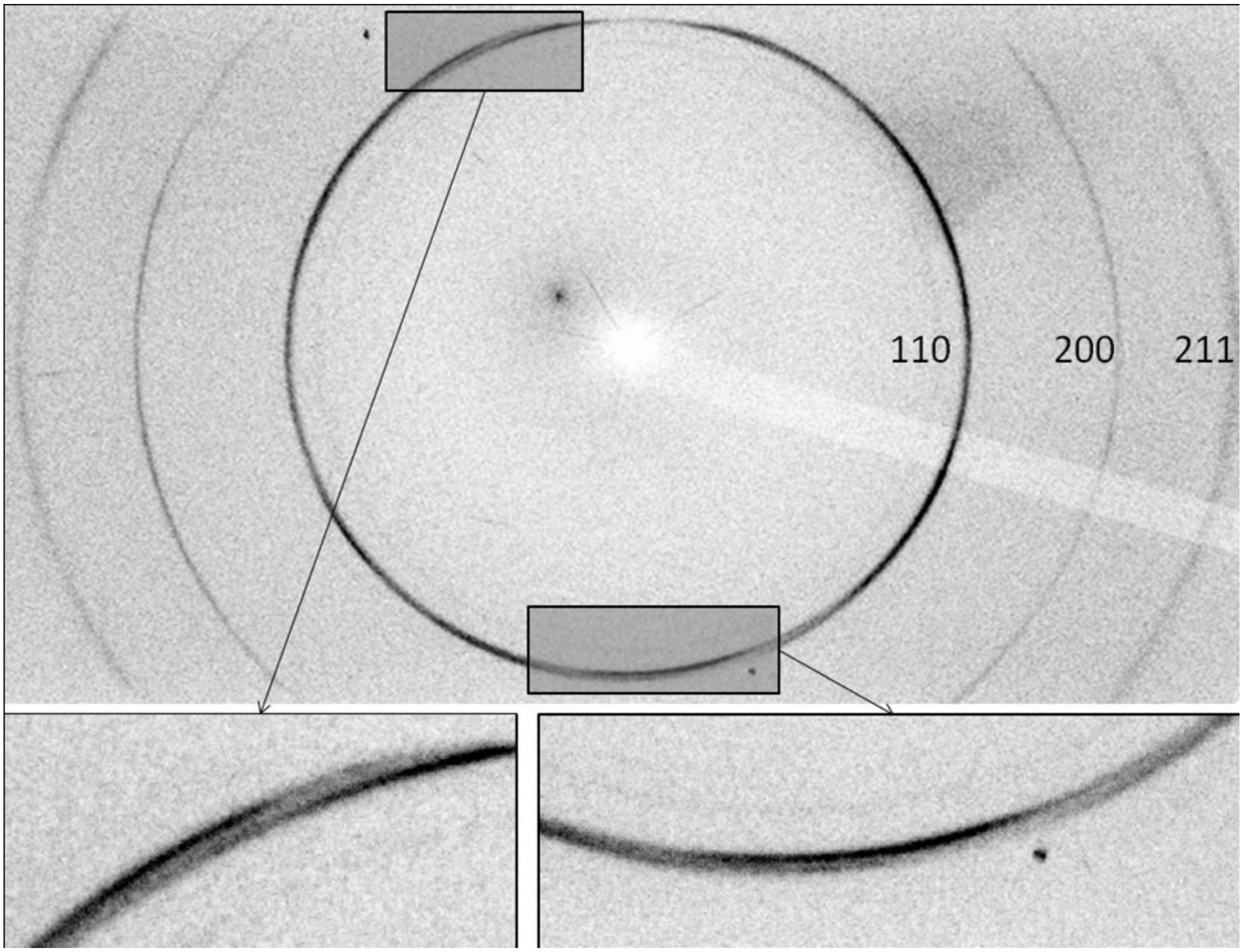

FIG. 3. 2D x-ray diffraction pattern recorded with MAR345 image plate of vanadium compressed under non-hydrostatic conditions at 82 GPa. The rings are indexed corresponding to the low pressure bcc phase. Magnified inserts at bottom show the splitting of the 110 peak.

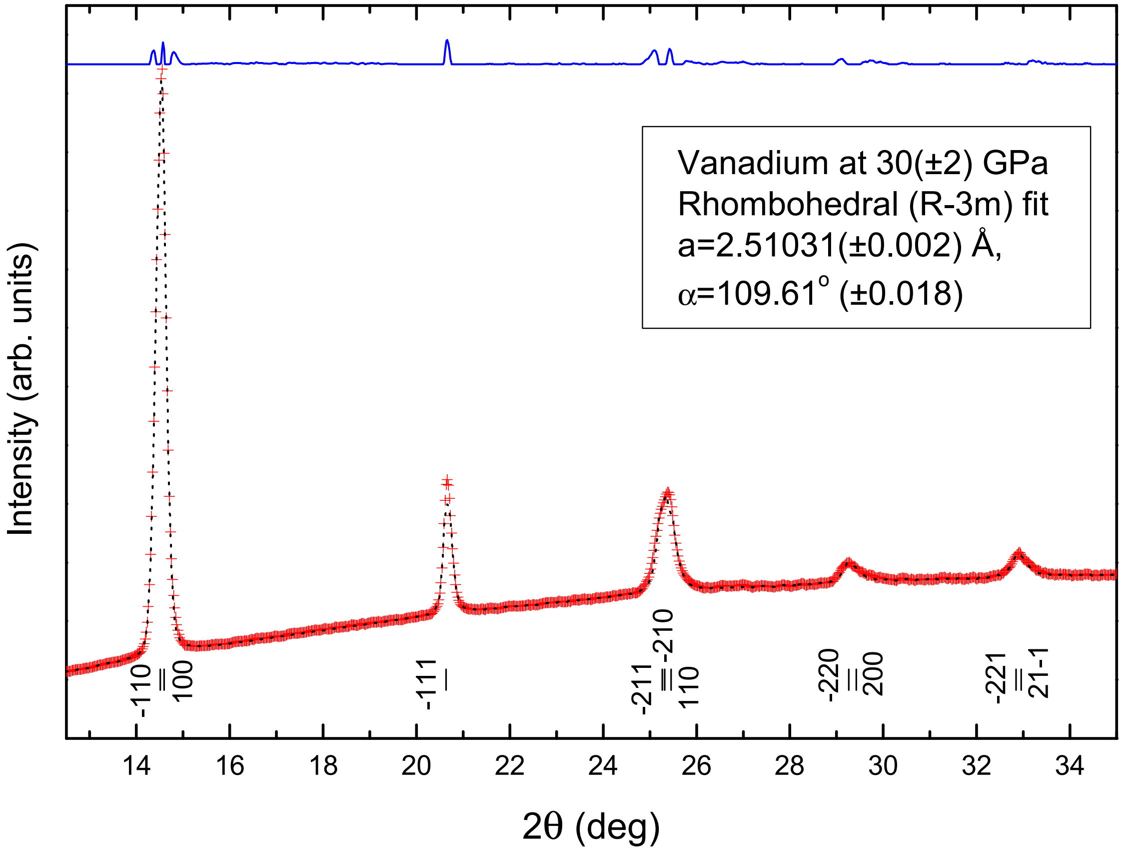

FIG. 4. (Color online) Rietveld refinement of integrated XRD pattern collected from sample compressed without pressure media at 30(±2) GPa. Red + experimental data, dashed line fit to the rhombohedral structure model, blue line residual to the fit (λ=0.51822Å).

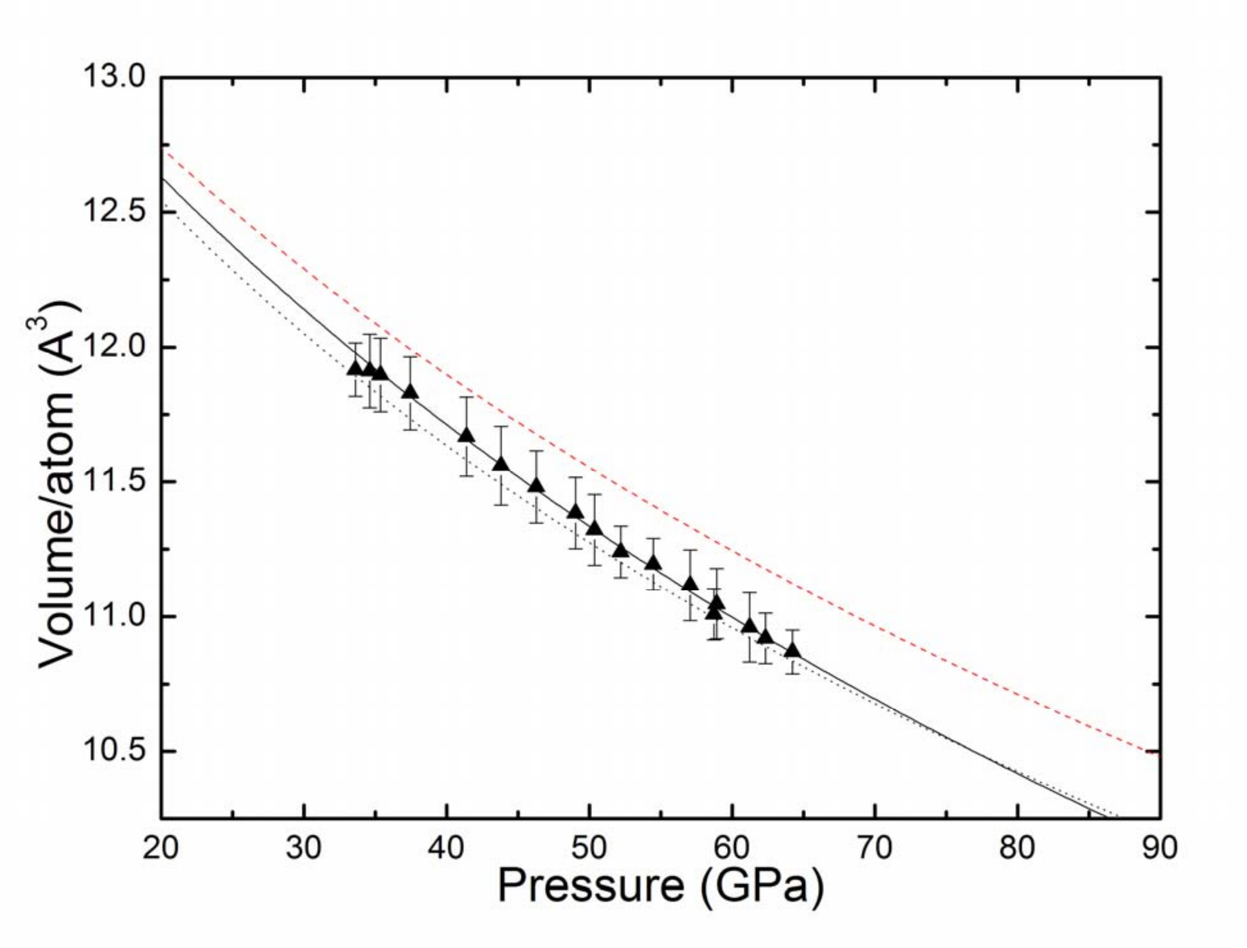

FIG. 5. (color online) Vanadium unit cell volume as a function of pressure, full triangles, compressed in Ne. Solid black line fit to the Vinet EOS with K_0=179(±8) GPa and K_0'=3.11(±1.23); dashed (red) line non-hydrostatic, dotted black line hydrostatic EOS from Ref.5.