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Theoretical confirmation of a high-pressure rhombohedral phase in vanadium metal

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Abstract

Recent diamond-anvil-cell (DAC) experiments revealed a new phase in vanadium metal at high pressure. Here we present results from first-principles electronic-structure calculations confirming the existence of such phase. The new phase is due to a rhombohedral distortion of the body-centered-cubic (bcc) ambient-pressure phase. The calculated transition pressure of 0.84 Mbar and density compare favorably with the measured data. Interestingly, a re-entrant bcc phase is discovered at an ultra high pressure, close to the limit of DAC experimental capabilities, of about 2.8 Mbar. We show, extending prior work, that the phase transitions in vanadium are driven by subtle electronic-structure effects.

It was proposed in theoretical studies that vanadium should become mechanically unstable in its ground state bcc phase at sufficiently high pressure [1, 2], and this transition was attributed to a Fermi surface nesting mechanism occurring during hydrostatic compression [2]. Electronic-structure calculations within density functional theory (DFT) were shown to predict a negative shear elastic constant, C_{44} , at megabar pressures, although a specific crystal structure resulting from the instability was not proposed [2].

This finding motivated a renewed interest in vanadium, and DAC measurements [3] recently confirmed that vanadium indeed is unstable in its cubic phase. Ding *et al.* concluded that, at pressures starting in the 0.6 – 0.7 Mbar range, a rhombohedral transition that corresponds to an increased angle (α) between the primitive unit-cell vectors spanning the bcc crystal occurs. They found the rhombohedral phase is stable up to the highest pressure studied, 155 GPa. An earlier DAC study under hydrostatic conditions reported that the bcc cubic phase remained stable up to 154 GPa [4]. Further calculations are needed to understand the difference between two DAC experiments, and confirm the presence of transition and other stable phases than the bcc phase.

In this Letter, we address the phase stability in vanadium metal up to and beyond the heretofore measured pressure. Specifically, we apply DFT in combination with a gradient-corrected exchange and correlation energy functional[5] as implemented in the Vienna Ab-initio Simulation Package (VASP) code along with the projector augmented-wave (PAW) method [6] and standard computational parameters [7].

Because the instability is believed to be linked to a shear distortion defined by C_{44} [2] we apply a generalization of the conventional [8] distortion used by Landa *et al.*:

$$T(\delta) = \begin{pmatrix} 1 & \delta & 0 \\ \delta & 1 & 0 \\ 0 & 0 & \frac{1}{1-\delta^2} \end{pmatrix}, \quad (1)$$

where δ parameterizes the distortion. The limitation of this particular strain is that it corresponds to orthorhombic symmetry, and thus does not allow for a rhombohedral distortion. Instead, the rhombohedral lattice system is obtained by applying a strain in the three-fold direction, and determined by a single lattice constant and an angle α made by any two axis

vectors. The volume-conserving bcc \rightarrow rhombohedral transformation matrix is defined as

$$T(\delta) = \begin{pmatrix} k & \delta & \delta \\ \delta & k & \delta \\ \delta & \delta & k \end{pmatrix}, \quad (2)$$

where k is determined from the real positive solution of $\det(T) = 1$ to ensure a volume-conserving transformation. The small displacement δ represents the amount of rhombohedral deformation of the bcc crystal: a positive δ corresponds to a decrease in α from the bcc value of $\alpha_0=109.47^\circ$. As we are exploring relatively small distortions, the normalizing factor k is always close to 1.

The volume-conserving rhombohedral transformation described in Eq. (2) does not result in strictly constant pressure. The total energy along the deformation path can be corrected from an internal energy to an enthalpy in order to investigate phase stability at constant pressure. For small δ , the enthalpy at pressure $P_0 = P(\delta = 0, V_0)$ may be calculated to a good approximation from the internal energy using the formula

$$H(\delta, P_0) \approx U(\delta, V_0) + P_0 V_0 - \frac{1}{2B(\delta, V_0)} \Delta P(\delta, V_0)^2 V_0, \quad (3)$$

where $\Delta P(\delta, V_0)$ is the pressure change at the given volume V_0 due to the rhombohedral transformation δ , i.e. $P(\delta, V_0) - P_0$. B is the bulk modulus at the given volume. The internal energy differences are small, but nonetheless, it turns out that the correction is not significant, and the internal energy may suffice to study phase stability.

In Fig. 1 we show the calculated enthalpies, as a function of the rhombohedral distortion, for various pressures. Already at about 0.73 Mbar, a metastable rhombohedral phase develops and becomes the ground state at ~ 0.84 Mbar with the corresponding α angle of 110.25° . The negative sign of the strain parameter δ reflects an increase in α relative to the cubic phase. Between 1.03 Mbar and 1.12 Mbar, another rhombohedral local minimum with a positive value of δ appears, resulting in three local minima including the bcc phase. At roughly 1.19 Mbar, the bcc phase becomes thermodynamically unstable, but remains mechanically stable, i.e. the curvature of the strain energy curve is still positive. This metastability is a phenomenon that has not been observed in the case of the simple orthorhombic shear due to Eq. (1), in which the strain-energy curve is essentially symmetric for small strains. Also at this pressure, the second rhombohedral phase with a positive δ takes over the first

rhombohedral phase and becomes the ground state. This trend persists up to a substantially higher pressure, and at 2.49 Mbar, the first rhombohedral phase completely disappears, and the second rhombohedral phase is the only mechanical and thermodynamical stable phase. The second rhombohedral phase with a positive δ value is most prominent at 1.87 Mbar, i.e. deepest enthalpy valley, with α of 108.14° . As the pressure is further increased, the ground state finally reverts back to the bcc phase at ~ 2.8 Mbar, and at 3.15 Mbar, the bcc phase becomes the only mechanical and thermodynamical stable phase. It is interesting to note that there are two competing rhombohedral phases with the opposite sign for the change in α .

With regard to the shear instability, we find that the bcc phase is mechanically unstable with a negative C_{44} from 1.41 to 2.49 Mbar, in good agreement with the results of Landa *et al.* [2]. The fact that the pressure range of the shear instability is completely contained within the range of the stable rhombohedral phase is suggestive of subtle electronic effects beyond the orthorhombic C_{44} shear instability. Even at ambient pressure, there is a pronounced asymmetry in the enthalpy curve for δ of -1.5 to -2%. This asymmetry persists throughout the entire pressure range examined, indicating that Lifshitz transition is irrelevant. The rhombohedral distortion produces an energy lowering, but the change is smaller than the elastic increase at ambient pressure. However, it becomes noticeable as the shear softening further develops, and finally becomes the ground state. When C_{44} is negative, there is a combined effect of the rhombohedral stabilization and the shear instability at the bcc phase, leading to the prominent rhombohedral phase. Thus it is natural to see the stable rhombohedral phase before entering and after exiting the region of shear instability as pressure is increased.

The rhombohedral transformation changes the band energy in two mechanisms; the density of states (DOS) broadening and DOS redistribution. The broadening is due to the split of degenerate bands coming from the reduced symmetry of the rhombohedral lattice. The broadening increases as δ is increased, and the amount of broadening together with the redistribution determines the location of rhombohedral local minima. The lower energy of the rhombohedral phase due to the latter effect can be explained in terms of the chemical bond. If we consider the decomposition of the $3d$ band contribution to the DOS into the five components, d_{z^2} , d_{xz} , d_{yz} , d_{xy} , and $d_{x^2-y^2}$, we find sharp features for $\delta=0$ in the partial DOS (PDOS) near the Fermi level, as indicated in Fig. 2. The shape of these features is

changed, lowering the energy, in the rhombohedral structure with increasing δ . The change is especially pronounced in the d_{xy} , d_{yz} and d_{xz} PDOS at 1.87 Mbar compared to ambient pressure, and can be interpreted as forming more stable bonds in terms of energy. In other words, d -electrons are redistributed to lower the band energy for the given bond angle change (directionality) due to the rhombohedral transformation as well as the bond length change due to the isotropic pressure. Since this is related to the directionality of bonds, it is not surprising that two shear deformation paths, orthorhombic shear and rhombohedral, show a similar trend but a different degree: it might be possible to find the true ground state from the combination of the two. It is not surprising either that a positive δ and a negative δ result in a significant asymmetry for the rhombohedral distortion.

It is difficult to discern whether the transition is first-order or second-order, but it is likely to be observed as a second-order transition at finite temperature, where the detailed profile of the enthalpy curve (Fig. 1) would likely be overshadowed by thermal fluctuations. Rather, only the overall anharmonicity would be observed and the phase change would appear gradual as reported in the recent experimental work [3]. The order parameter at zero temperature is plotted in Fig. 3; ‘bcc phase’ represents the ambient ground state, and ‘stable phase’ stands for a mechanically stable yet thermodynamically unfavorable local minimum against for the notion of ‘ground state’. The overall tendency is a larger and abrupt change in the order parameter than that of experiments, which may not be captured at finite temperature considering that the thermal effects on the order of $k_B T$ at room temperature are significantly greater than the enthalpy differences between stable phases at any given pressure.

The quoted theoretical transition pressures above are obtained from the calculated response to hydrostatic compression at zero temperature. In Fig. 4, we show our calculated equation of state together with data given by Ding *et al.* [3]. The data points are obtained from non-hydrostatic (NH) and quasi-hydrostatic (QH) pressures, where the open (solid) symbols refer to the bcc (rhombohedral) phase. The NH data were obtained from a vanadium sample loaded in the DAC chamber without a pressure medium, whereas for the QH data helium was used for this purpose. The QH data are noticeably different than the NH data and in better agreement with the calculations, as expected, since the calculations correspond to perfectly hydrostatic compression. For the QH measurements, the bcc \rightarrow rhombohedral phase transition takes place at a pressure of 0.59 Mbar and an atomic volume

of 10.99 \AA^3 . These results compare relatively well with the calculated transition pressure (0.84 Mbar) and volume (10.25 \AA^3), shown as a vertical line in Fig. 4. There is considerable sensitivity to the computational details in the calculated transition pressure; all-electron calculations [9], not relying on the pseudopotential assumption, predict the transition at 0.60 Mbar (10.78 \AA^3), in near perfect agreement with the experimental data.

It is interesting to notice that the second rhombohedral phase with a positive value of δ , which becomes the ground state at a slightly lower pressure than the highest NH pressure studied, was not found in the experiments. It is likely due to the difficulties in maintaining hydrostatic conditions in the DAC, but it might as well be that the effective transition pressure from one rhombohedral phase to the other is altered at finite temperature, and has not been reached by the experiments.

Another effect that can differentiate the experimental measurements from our calculations, and one experiment from the other, is the purity of the specimen. We have found that a small inclusion of chromium ($\text{V}_{0.9}\text{Cr}_{0.1}$) substantially changes the energy, and diminishes the electronic effects driving the rhombohedral stabilization as shown in Fig. 5. The stabilization is alternatively accomplished by moving the Fermi level itself in the alloy. It is simple to illustrate this phenomenon for V-Cr alloy, since Cr is the neighbor and a rigid-band model should be applicable. Hence one can simply apply the virtual-crystal approximation in the case of Cr in the V; nevertheless the stabilization effect is more general and could have a similar influence on other metals such as Nb[2].

We have confirmed the existence of a rhombohedral phase in vanadium metal as recently suggested by high-pressure DAC experiments. The calculated stability of this new phase ranges from about 0.84 Mbar up to a predicted 2.8 Mbar. The primary reason for the instability is pressure-induced Fermi surface effects that have been discussed in detail in our earlier publications [2]. At ultra-high compression, the $3d$ bands broaden due to an increase in orbital overlap, and the electronic instability vanishes, thus restoring the bcc phase in vanadium. This example of a cubic \rightarrow distorted phase \rightarrow cubic is uncommon in an elemental metal.

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Figures

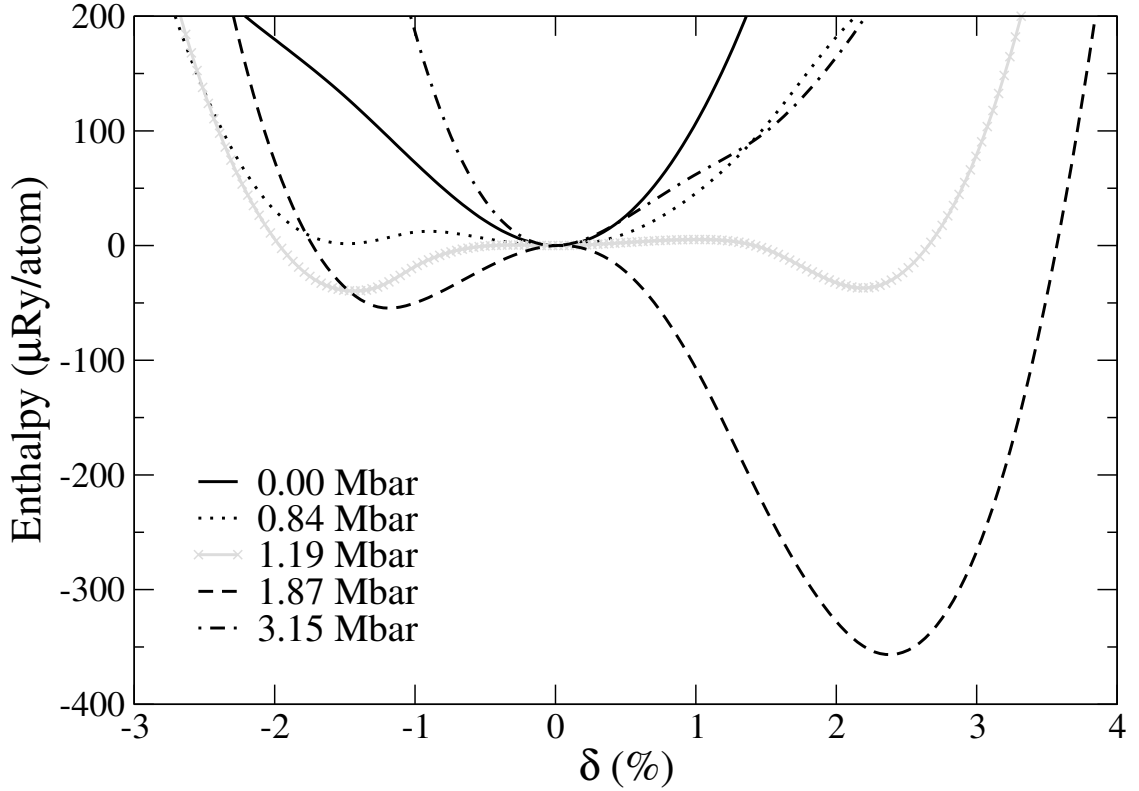


FIG. 1: Enthalpy as a function of δ . The pressure is in units of Mbar.

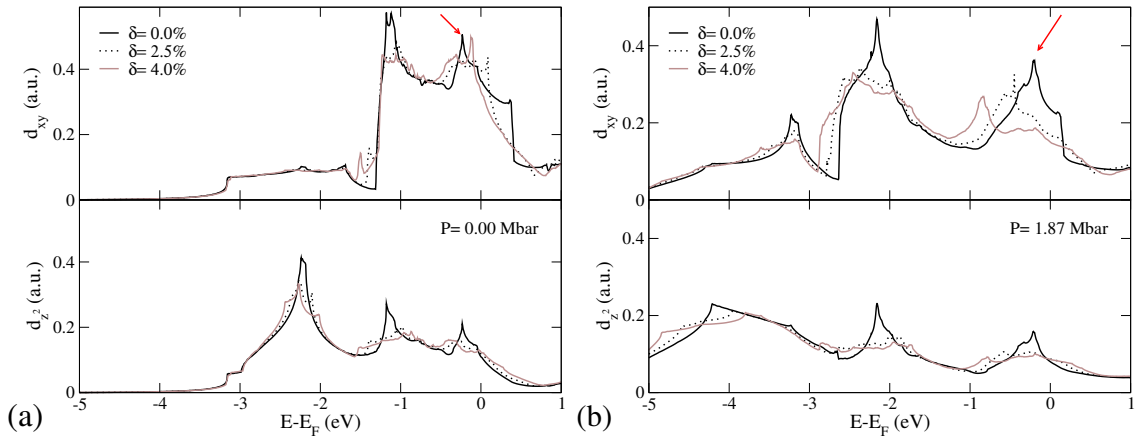


FIG. 2: The 3d partial density of states (PDOS) (a) at ambient pressure, and (b) at 1.87 Mbar. Only d_{xy} and d_{z^2} are shown, but d_{xz} and d_{yz} are, although not necessarily in principle, almost identical to d_{xy} , and $d_{x^2-y^2}$ to d_{z^2} respectively to the accuracy of our calculations.

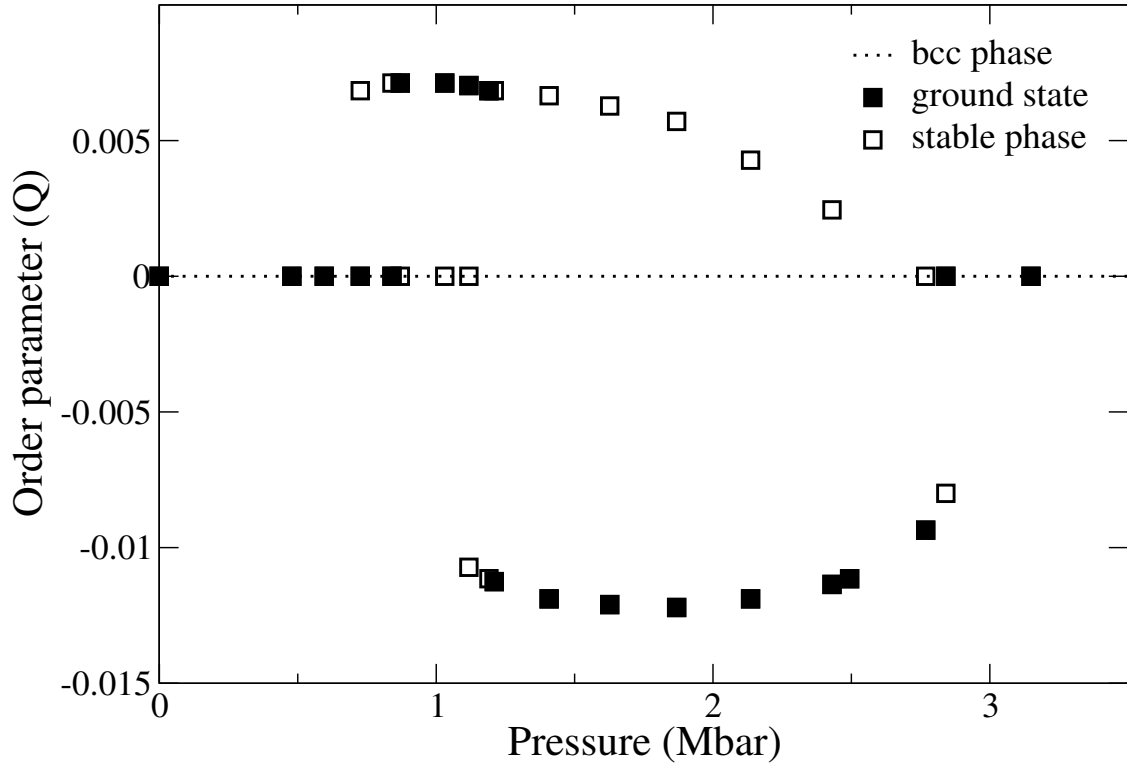


FIG. 3: The order parameter of stable phases under pressure. The order parameter is defined as $Q = \alpha/\alpha_0 - 1$, where $\alpha_0 = 109.47^\circ$ is the axis angle of the bcc phase.

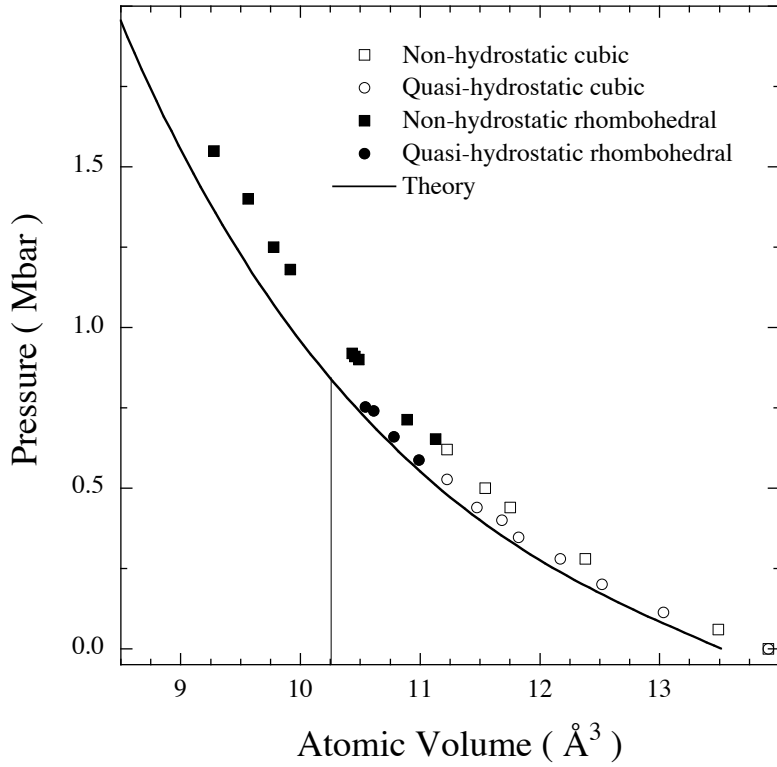


FIG. 4: Experimental data from Ding *et al.*[3] together with present theory (full line). The calculated bcc \rightarrow rhombohedral transition volume (10.25\AA^3) is marked with a vertical line.

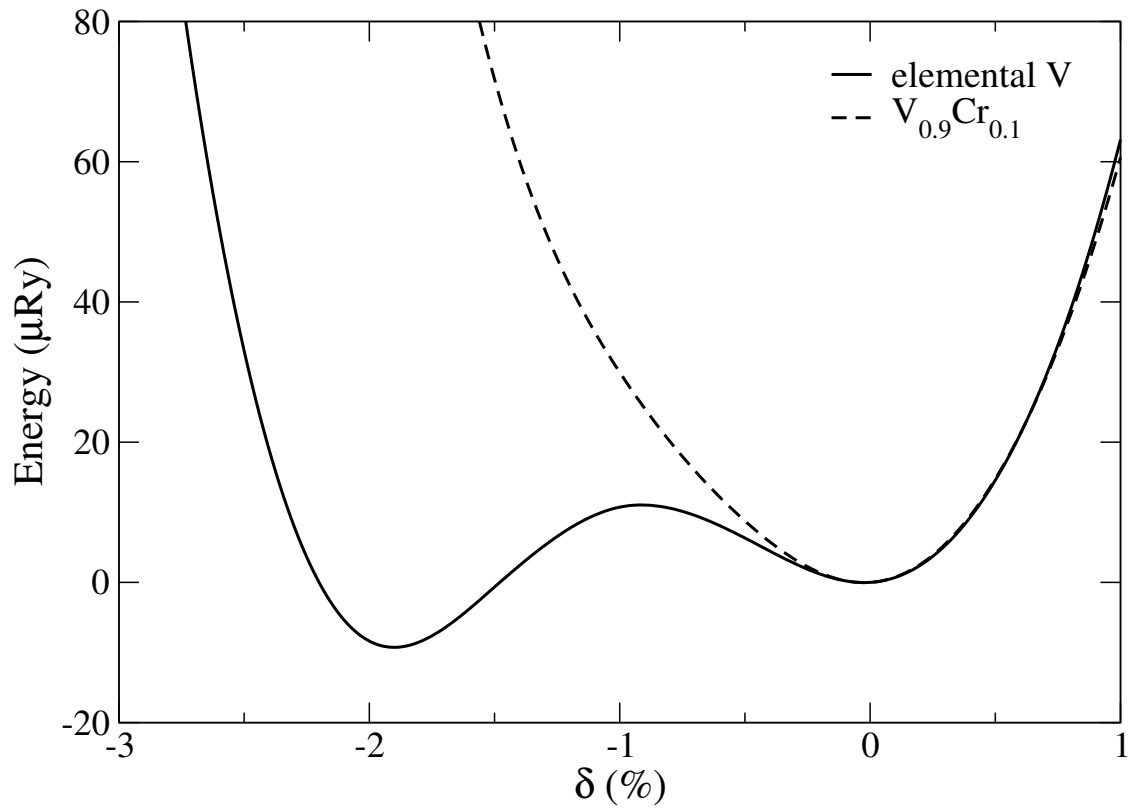


FIG. 5: All electron calculations showing the effect of Cr inclusion on the energy at 0.63 Mbar.