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Effects of changes in the translational symmetry of VRu on the electronic density of states

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Abstract. Effects of the increase of the translational period of the VRu crystal structure on the density of states (DOS) at the Fermi level are investigated by means of first-principles band structure calculations (LMTO–ASA method) by using different types of model structure. The results reveal that the DOS of equiatomic VRu at the Fermi level is very sensitive to the changes in the translational symmetry of the crystal. Moreover, our calculations show that the increase of the translational period of the crystal structure is one reason for the considerable reduction of the DOS at the Fermi level giving one possible explanation for the observed drastic changes in physical quantities related to the DOS at the Fermi level. We have also investigated the effect of the observed crystal modulation parallel to the (100) plane of the normal tetragonal structure of VRu.

1. Introduction

Macroscopic properties of materials are induced by interactions between their microscopic constituents, electrons and ions. Thus in order to design new materials having specific properties or to understand the properties of materials under different conditions one has to be able to determine the microstates of the corresponding system. Unfortunately, there is no practical way to solve this problem exactly. The best we can do is to use some approximate quantum mechanical method to solve the properties of the many particle system composing the material under consideration.

Elasticity, crystal structure, specific heat, magnetism etc all depend on the electronic structure of the considered system. However, the actual situation is even more complicated than stated above. The macroscopic properties of the system also affect its microscopic properties requiring a self-consistent solution to the problem. For instance, the crystal structure of the considered system has a significant influence on its electronic structure and vice versa. Compounds and alloys usually have complicated crystal structures, which have been difficult to treat theoretically. Fortunately, the recent development in numerical techniques and computer technology has made it possible to extend the scope of first-principles calculations for the realistic structures of multicomponent alloys and compounds as well.

The drastic change in the physical properties of equiatomic VRu alloys in the phase transition from a high temperature cubic structure to a low temperature tetragonal structure has been a puzzle for a long time. This structural transition is accompanied with large

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changes in magnetic susceptibility, electrical resistivity, specific heat, Knight shift and spin–lattice relaxation rate of ^{51}V [1]. Chu *et al* and Asada *et al* suggested that these experimental observations result from a large reduction in the electronic density of states (DOS) at the Fermi level in the cubic to tetragonal transition [1, 2]. Surprisingly, the calculations of Asada *et al* [1] show that the Fermi-level DOS ($N(E_F)$) in tetragonal VRu is larger than that in cubic VRu. This contradictory result has been an unresolved problem since then. In the present work we suggest one possible explanation to this problem.

Ohnishi *et al* [3] have shown that in the cubic to tetragonal transition VRu has a rather complex crystal structure. The observed crystal structure is split into several domains thus breaking the simple tetragonal translational symmetry of a VRu crystal. Because the translational symmetry of the crystal determines the shape and the extent of the Brillouin zone, it is natural to assume that changes in translational symmetry affect the band structure and DOS at the Fermi level. The increasing of the length scale of the translational periodicity of the crystal structure has been shown to lead to drastic changes in $N(E_F)$ in other binary metallic alloys [4, 5]. In the present work we use a band structure calculational method to investigate effects of changes in the translational symmetry of VRu on the DOS at the Fermi level. To simulate the cubic to tetragonal transition in VRu we use in the calculations model structures which are either simple orthorhombic type (in the case of the first kind of anti-phase boundary; non-symmorphic space group D^5_{2h}) or simple tetragonal type (space group D^1_{4h}).

2. Methods of calculations

The calculations were performed by using the scalar-relativistic linear muffin-tin orbital (LMTO) method including the combined correction terms and the atomic-sphere approximation [6, 7]. The basis-function set for the valence electrons consists of s, p and d functions. The combined correction terms are introduced to correct both for the approximations in the interstitial region (i.e. in the region between the MT spheres) and for the neglect of higher l partial waves [7]. The exchange–correlation effects were introduced within the local density approximation using the von Barth–Hedin potential [8]. The core states were held fixed throughout the self-consistent cycles of the valence electrons (frozen-core approximation). The same atomic Wigner–Seitz radius was used both for V and Ru. This is a very reasonable approximation, because the difference of the atomic Wigner–Seitz radii of elemental Ru and V is less than 1%. The lattice parameters used in the calculations (for the ideal binary compounds without defects) are $a = b = 2.927$ Å and $c = 3.123$ Å for the tetragonally distorted B2 type cell ($L1_0$, CuAu) and $a = 2.977$ Å for the cubic B2 type cell (CsCl) [1]. At first we made test calculations for the biggest unit cell used in the calculations (32 atoms). Guided by the results of the test calculations we adjusted the calculational parameters to obtain well converged DOS curves. The final results of the biggest cell were calculated using 108 k points in the irreducible wedge of the Brillouin zone by the linear tetrahedron method. In calculations of smaller cells we used more k points (384 at maximum). In the real and reciprocal lattice sums we used more than 1000 vectors.

3. Results and discussion

We begin by comparing our results with those of Asada *et al* [1]. Asada *et al* calculated the DOS at the Fermi level for simple cubic and simple tetragonal structures. They obtained

20.7 and 24.3 states Ryd^{-1}/atom for simple cubic and tetragonal VRu, respectively. Our results for the same quantities are 21.9 and 25.6 states Ryd^{-1}/atom. So, there is a good agreement between these results; in particular the obtained increase of $N(E_F)$ due to the tetragonality is practically the same in both investigations. However, according to Ohnishi *et al* [3] the structure of VRu near the transition temperature differs considerably from the simple cubic and simple tetragonal structures.

In the following we describe briefly the structural transformation in the considered cubic to tetragonal transition. This transition consists of several steps and a sequence of complex crystal structures appears. The high-temperature cubic B2 type phase of VRu transforms at lower temperatures to the tetragonally distorted B2 type structure. According to Ohnishi *et al* [3] this low-temperature tetragonal structure has two types of modulation, commensurate and incommensurate modulations. Ohnishi *et al* investigated only the incommensurate modulated structure, because it is reasonable to suppose that the incommensurate modulation is more relevant for the understanding of the cubic to tetragonal phase transition [3].

The structure of the incommensurate modulated low-temperature tetragonal phase is shown in figure 1(a). The incommensurate modulated structure is composed of commensurate domains of pseudo-tetragonal structure (γ is not 90° exactly) separated by incommensurate regions. Ohnishi *et al* [3] have fitted their experimental data to a mathematical model describing the incommensurate modulated tetragonal structure. This model can be used to calculate the atomic positions within this structure (cf equations (1), discussed later). As the phase transition proceeds the commensurate domains grow. At lower temperatures the incommensurate structure transforms to a commensurate (pseudo-tetragonal) structure with twinning. The twin structure is composed of twin lamellae with the commensurate modulated (pseudo-tetragonal) structure lying parallel to the (011) plane (figure 1(b)). The thickness of the twin lamellae varies from 2 nm to 5 nm. The tetragonally elongated c axes of the neighbouring twin lamellae are oriented nearly perpendicular to each other.

Due to the complexity of the crystal structure of equiatomic VRu alloys in the cubic to tetragonal phase transition [3] the direct numerical simulation of this phase transition by using the present day first-principles computational techniques is unfortunately impossible. In the present work we used simplified crystal structures which will be discussed in the following. The structures used in the calculations retain the essential features of the symmetry of the observed crystal structure of VRu. In our model calculations the length of the periodicity of the crystal is of the same order of magnitude as that in the experimentally observed twin lamellae structure. We used coherent interfaces between different domains. The tetragonally elongated c axes is in the same direction on both sides of the interfaces, because of the coherency of the interfaces. Our aim was to investigate the effects of the changes in the translational symmetry of the VRu crystal on $N(E_F)$.

Our main target was to simulate the tetragonal (or pseudo-tetragonal) twin structure. We started this by using the cubic structure with first kind anti-phase boundaries perpendicular to the [011] direction to see the effect of the increasing of the translational period of VRu in the [011] direction. To investigate the effect of different approximations related to the structure considered in our simulations several calculations were performed using tetragonal and pseudo-tetragonal structures. To change the long-range order of the crystal and to simulate boundaries caused by twin structure we used different types of boundary: anti-phase boundaries and local elongations in one crystal direction. Long-period superstructures consisting of successive anti-phase domains of definite size have been found experimentally in binary alloys [9, 10]. Moreover, the anti-phase boundary is a reasonable choice in our case, because the atomic arrangement has a regular out-of-step relation across the twin boundaries in VRu [3].

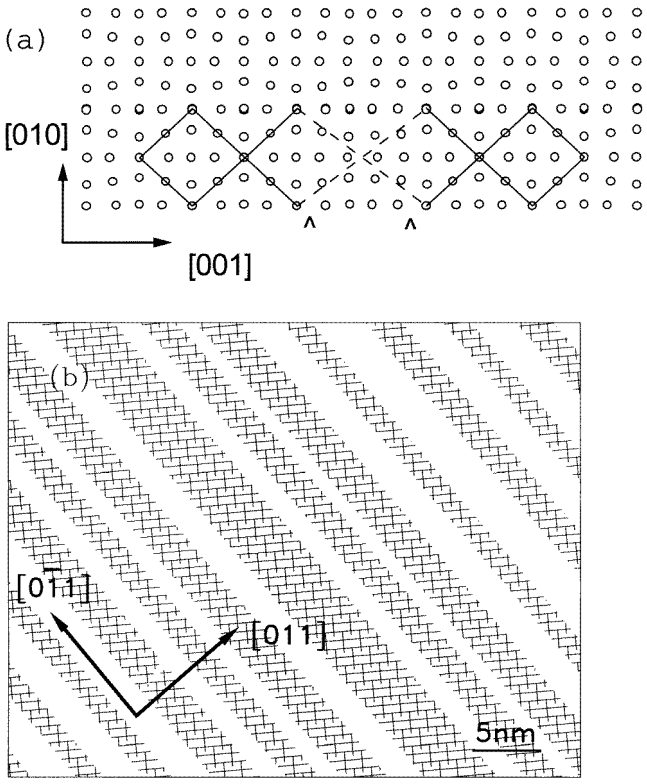

Figure 1. (a) Schematic model of the incommensurate modulated structure which is composed of domains of the commensurate modulated structure [3]. Arrows mark the boundaries of the commensurate domains. Squares indicate the unit cell of the commensurate modulated or pseudo-tetragonal structure (γ is not exactly 90°). Only vanadiium atom positions are shown. (b) Schematic model of the twin structure (cf figure 8 in [3]). The twin lamellae (white and hatched areas) lie parallel to the (011) plane. The structure type inside the twin lamellae is pseudo-tetragonal.

There exist two types of anti-phase boundary which are called first kind and second kind anti-phase boundaries. The anti-phase boundary is called the first kind, when the out-of-step vector lies in the boundary plane [9, 10]. In order to create the second kind anti-phase boundary, one has to remove or insert one or more atomic layers [10]. To investigate the effect of the formation of the periodic domain structure in VRu, long unit cells (12.4–37.5 Å) were used in the present work. The amount of the atoms in the unit cell varies from 12 to 24. We treated all V (Ru) atoms as equivalent atoms in long-period structure calculations. The inequivalency of the atoms has only negligible effect on $N(E_F)$ (less than 1%).

To simulate the commensurate twin structure of VRu in the cubic to tetragonal phase transition we first consider a cubic crystal structure. The length of the primitive translational period along the [011] direction was varied by modulating the crystal structure by a sequence of first kind anti-phase boundaries of different domain length perpendicular to the [011] direction. The lattice parameters of the unit cell without anti-phase boundaries are $\sqrt{2}a$ and a with respect to the B2 type unit cell. Figure 2 shows that the change in the translational symmetry of the VRu crystal drastically decreases $N(E_F)$. The maximum reduction in $N(E_F)$ is more than 20%.

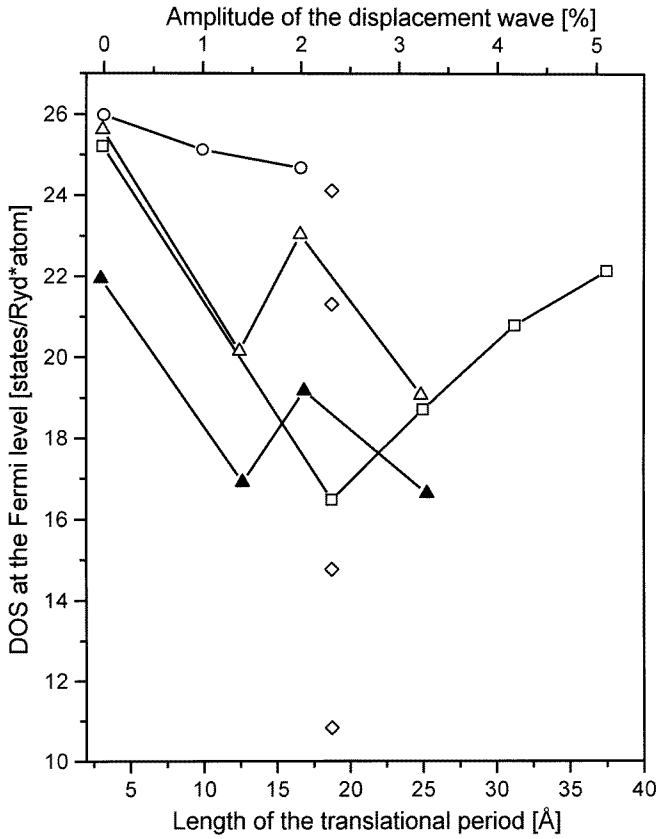

Figure 2. DOS of equiatomic VRu at the Fermi level as a function of the length of the translational period of the crystal obtained by using different types of crystal boundary. The DOSs of tetragonal structures are shown by white symbols and the DOSs of cubic structures are shown by black symbols: first kind anti-phase boundary (triangles), second kind anti-phase boundary (squares), local elongation with different coefficients of the elongation: 1.03, 1.05, 1.10 and 1.15 from top to bottom (diamonds). The DOS of the pseudo-tetragonal structure is represented as a function of the amplitude of the displacement wave d_0 (circles) (upper x-axis).

In order to estimate the effect of the different approximations involved in the construction of the crystal structure used in our previous calculation, several calculations for different structures were performed. The effect of the tetragonality ($c/a = 1.067$) of the crystal was tested by taking the first kind anti-phase boundaries to be perpendicular to the [110] direction instead of the [011] direction. In this new construction the tetragonality of the crystal structure does not produce any additional complications and the resulting unit cell has practically the same size as in the previous case. As figure 2 shows, the obtained increase of $N(E_F)$ due to the tetragonality depends only slightly on the length of the translational period of the crystal supporting the earlier observations [1] that the tetragonality itself has only a minor effect on $N(E_F)$ in the cubic to tetragonal transition. This suggests that the large reduction in $N(E_F)$ due to the formation of the long-period domain structure in VRu is of a more fundamental type and it can be investigated by using basic crystal structures, which differ in their short-range forms, e.g. cubic, tetragonal or pseudo-tetragonal. Some long-period unit cells used with the first and second kind anti-phase boundaries are shown in figure 3.

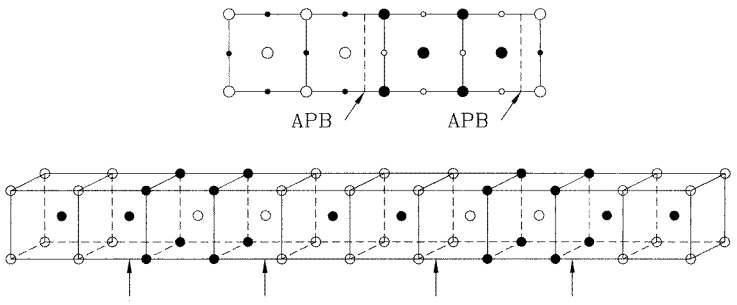

Figure 3. Long-period unit cells of the first and second kind anti-phase structures consisting of 16 and 20 atoms, respectively. The unit cell of the first kind anti-phase structure is projected onto the (100) plane. White and black spheres refer to the V and Ru atoms, respectively. Large and small spheres refer to atoms in different atomic planes. The positions of the anti-phase boundaries are marked by arrows.

Instead of the cubic or tetragonal structure used in the calculations explained above the basic structure in the twin lamellae is of a commensurate modulated or pseudo-tetragonal type with the lattice parameters $A = B = 2(a^2 + c^2)^{1/2}$ and $C = a$, where a and c are the lattice parameters of the simple tetragonal cell [3]. The atomic positions on the crystal planes perpendicular to the [100] direction can be expressed as

$$\begin{aligned} y &= y_0 + (-d_1 + d_2)\sin\Theta \\ z &= z_0 + (d_1 + d_2)\cos\Theta \\ d_1 &= d_0 \sin[q_1(y_0\cos\Theta + z_0\sin\Theta)] \\ d_2 &= -d_0 \sin[q_2(y_0\cos\Theta - z_0\sin\Theta)] \\ \tan\Theta &= 2c/(2a + \Delta) \end{aligned} \tag{1}$$

where y_0 and z_0 are the original coordinates, q_1 and q_2 are the wavenumbers and d_0 is the amplitude of the displacement wave. Δ defines the incommensurability (for commensurate structure $\Delta = 0$). According to Ohnishi *et al* [3] d_0 between 1% and 2% gives the best fitting to the experimental data. To study this pseudo-tetragonal structure numerically we used a 32-atom orthorhombic unit cell. The atoms of the unit cell were divided into seven inequivalent classes depending on the atomic type and the local environment of the atom. The atomic arrangement projected onto the (100) plane is represented in figure 4. In figure 2 we show the corresponding calculated results for the Fermi-level DOS of this pseudo-tetragonal structure using the displacement amplitudes $d_0 = 0\%$, 1% and 2%. The modulation decreases $N(E_F)$, but the obtained decrease (about 3–5%) is much less than the reduction due to the introduction of long-period domain structures in the crystal structure. The results for the pseudo-tetragonal structure support the conclusion drawn from our previous calculation that the short-range order has only a minor effect on the phenomenon under consideration.

The crystal structures of different lamellae are connected incoherently across the twin boundaries. The exact atomic positions at the twin boundaries are not known. However, as we see from the calculations for the pseudo-tetragonal structure using different amplitudes (0%, 1% and 2%) (figure 2), small changes in the atomic positions in the boundaries are expected to be unimportant compared to the change in translational periodicity. In the following we consider long-period structures with different types of domain boundary. Instead of the first kind anti-phase boundaries we introduced the second kind anti-phase boundaries perpendicular to the c axis in the tetragonal crystal structure. The results are shown in figure 2. The reduction in $N(E_F)$ is more pronounced (35%) than in the case

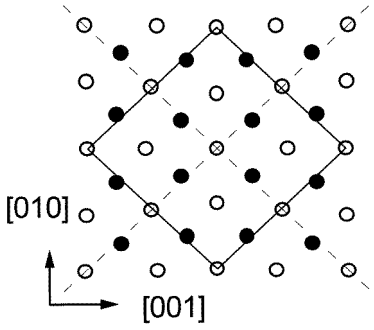

Figure 4. Atomic positions of the commensurate modulated or pseudo-tetragonal structure projected onto the (100) plane. The amplitude of the modulation is exaggerated and two diagonals are shown by dashed lines to make the modulation discernible in the figure. The unit cell of the pseudo-tetragonal structure is marked by a solid line.

of the first kind anti-phase boundary. This is, however, expected since the second kind anti-phase boundary creates a larger distortion in the crystal structure than the previously discussed first kind anti-phase boundary providing in this sense a better model for the actual boundaries in the twin lamellae structure. In this case, also, we studied the reduction of the $N(E_F)$ as a function of the thickness of the domains. The DOS at the Fermi level is found to increase monotonically with increasing domain thickness. This behaviour is natural since the local crystal environment inside the anti-phase domains is approaching the environment in the normal tetragonal structure as the thickness of the anti-phase domains increases. To show that the anti-phase boundaries are not the only boundary types which can produce the reduction in $N(E_F)$ we performed calculations using the tetragonal structure with boundaries made by a local elongation of the lattice parameter c. Figure 2 shows that such boundaries also reduce $N(E_F)$ suggesting that the reduction of $N(E_F)$ is obtained by various types of boundary, but the amount of the reduction depends on the details of the boundaries.

The overall shapes of the total DOS of the normal tetragonal strructure and of the first kind anti-phase structure are very similar as shown by figure 5. There appears a pseudogap between bonding and anti-bonding states. However, the DOS at the Fermi level has fallen considerably in the case of the first kind anti-phase structure. The local partial DOS reveal that the reduction is mostly due to the d DOS of V. We can explain this with the aid of the characteristic d-band energies (top, centre and bottom). The d band of V has shifted to higher energies and the d band of Ru has shifted to lower energies due to the formation of the long-period domain structure. Moreover, the DOS area of V is larger above the pseudogap than the DOS area of Ru. The total DOS consists mainly of d-type states. The obtained considerable reduction of $N(E_F)$ is possible because the DOS rises very rapidly at the Fermi level. Because of the steepness of the DOS curve one has to be very careful in numerical investigations. The reduction of the Fermi-level state density stabilizes the system [2, 11]. In the cases corresponding to the second kind anti-phase structure and locally elongated structure, the changes in the overall shapes of the total DOS are more pronounced and accompanied by larger reduction in the DOS at the Fermi level.

According to Chu *et al* the electronic specific heat coefficient γ of the equiatomic VRu decreases by 60% due to the structural phase transformation [2]. Because γ is proportional to $N(E_F)$ at 0 K we can compare our calculated results directly to the experimental data

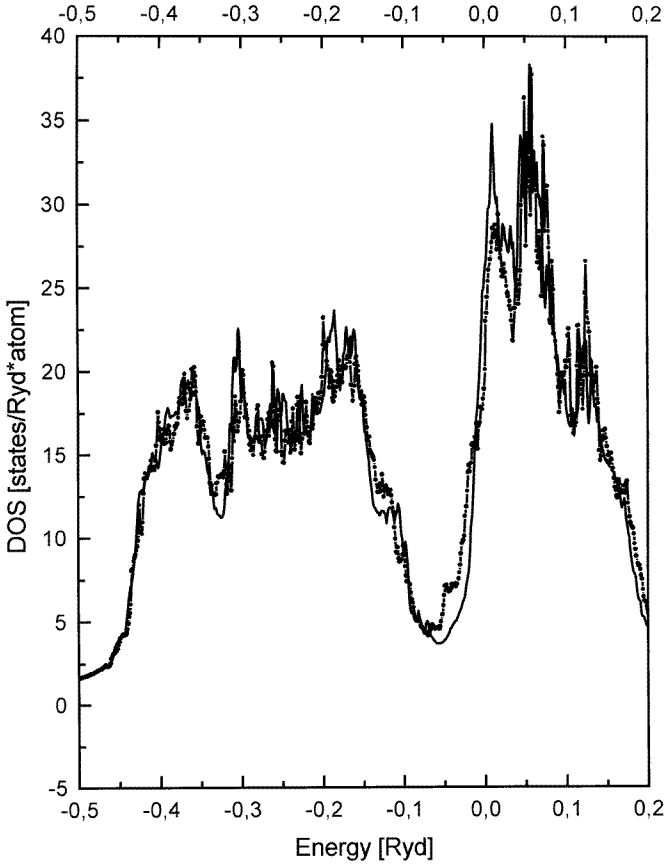

Figure 5. Total density of states of normal tetragonal structure (full curve) and first kind anti-phase structure corresponding to a length of the translational period approximately 25 Å (chain curve).

provided the electron–phonon mass enhancement factor $1 + \lambda$ does not change much with changes in the translational symmetry of the crystal [12]. This assumption is supported by the investigation of the specific heat of CuAu alloys [4]. As figure 2 shows the formation of the anti-phase boundaries in tetragonal VRu reduce $N(E_F)$ by about 25% at maximum compared to the cubic case. However, the long-period domain structure based on 15% local crystal elongation at the boundaries leads to about 50% decrease in $N(E_F)$. The decrease of calculated $N(E_F)$ is smaller than that experimentally detected. The main reason for this is probably the coherence of the interfaces of our model structures. Moreover, the thicknesses of different twin lamellae vary in VRu samples which changes the translational symmetry of the crystal even more. However, our results show that the increase of the translational period of the crystal structure of VRu decreases considerably the DOS at the Fermi level.

4. Conclusions

The density of states of equiatomic VRu at the Fermi level is very sensitive to the changes in the translational symmetry of the crystal. Our calculations show that the increase of the translational period of the crystal structure in the cubic to tetragonal transition is one reason

for the considerable reduction of the density of states at the Fermi level giving one possible explanation for the observed drastic changes in physical quantities related to the density of states at the Fermi level. The major changes in the density of states at the Fermi level are due to the long-period domain structure. The short-range order has only a minor effect.

Although the importance of the long-period structures in the cubic to tetragonal transition in VRu has become evident, more detailed data on the crystal structure are needed for more direct simulations of the electronic structure in this phase transition.

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