The modeling of phase formation and crystal structures is still a major challenge in solid-state chemistry [1–3]. A crystal structure may sometimes be guessed based on information from the chemical composition, the crystal structure of a neighboring phase and by applying chemical bonding concepts. However, only first-principles calculations effectively allow to model phase formation, crystal structures and disorder phenomena.

Recently, we have been able to model the phenomenon of preferential site occupation [4] for the ternary C14 Laves phase Nb(Cr1–xCox)2, which is formed in a large homogeneity range from 0.127(3) ≤ x ≤ 0.937(3) at 1100°C. The ansatz is based on the idea of computing the partition function \( Z_N \) for the Laves phase Nb(Cr1–xCox)2 using the ordered superstructures of NbCr1–xNCoN as an approximation. For a given \( N \) between 2 and 6, one has to consider all possible ways of distributing these \( N \) Co atoms among the crystallographic sites \( 2a \) and \( 6h \). If \( E \) denotes the total energy, \( p \) the number of Co atoms occupying the \( 2a \) site, \( M \) the number of symmetrically inequivalent configurations and \( g \) the multiplicity, then \( Z_N \) is given by:

\[
Z_N = \sum_{\sigma=1}^{N!} g_{N,p,\sigma} \exp(-E_{N,p,\sigma} / (k_B T)) \quad (1)
\]

In this case, the calculation predicts a preferential site occupation of the respective minority component on the \( 2a \) site and a site occupation reversal at approximately \( x = 0.5 \). The computed values are in good agreement with the experimental data.

Since it was possible to model the short range order in a ternary C14 Laves phase we have extended the computations to calculate the unit cell volume, the lattice parameters, the \( c/a \) ratio and the phase stability of C15 and C14 phases along quasibinary sections \( AB_2' \sim AB_2 \). The computed properties are suitable for multiple uses: (i) they help to minimize the number of required experiments along the section \( AB_2' \sim AB_2 \) because the computation predicts the general curve shape; (ii) in the case of the absolute values deviating from the experiment, the calculated values can be calibrated by a small number of experimental data; (iii) a system can be probed for unexpected behavior.

**Cell Geometry of Nb(Cr1–xCox)2**

The lattice parameters \( a \) and \( c \), the mean atomic volume and the \( c/a \) ratio have been calculated using the partition function in the same way as the site occupation factors. However, a supercell has been used to increase the number of compositional data points. First-principles total-energy calculations were performed with the Vienna Ab-Initio Simulation Package (VASP) [5] within the generalized gradient approximation (GGA) [6]. The calculated data as shown in Figure 1 are based on a \( 2 \times 1 \times 1 \) supercell, i.e., NbCr16–xNCoN with \( N = 1–16 \).

The calculated unit cell parameters are slightly smaller than the experimental data. The experimental and the calculated data for the mean atomic volume follow Vegard’s volume rule. Both data sets can be brought into conformance by adding the volume difference from one data point to the experimental data. The curve shape of the \( c/a \) ratio for C14 Nb(Cr1–xCox)2 can be described by an S-type behavior with the inflection point at \( x \approx 0.6 \) and the minimum at \( x \approx 0.8 \). The absolute values of the calculated \( c/a \) ratio are fitted to the experimental for reasons of clarity.

---

**Fig. 1:** Experimental and calculated \( c/a \) ratio for C14 Nb(Cr1–xCox)2. The calculated data are temperature scaled by using the experimental \( c/a \) ratio at the predicted minimum. The inset shows the calculated and the experimental mean atomic volume. The calculated data are not fitted to the experimental for reasons of clarity.
culated c/a ratio differ from the experimentally obtained values. However, the general S-shape, the location of the inflection point and the minimum and maximum are well captured. The calculated c/a ratio curve can be fitted to the experimental values by changing the temperature $T$ in Eq. 1 using the c/a ratio at the predicted minimum.

### Phase Stability of Nb(Cr$_{1-x}$Co$_x$)$_2$ and Ta(V$_{1-x}$Fe$_x$)$_2$

In order to determine the composition dependent stability of the C14 and the C15 structure type along the section NbCr$_2$–NbCo$_2$, the Gibbs energy $\Delta G$ has been calculated. For cubic C15, Nb$_8$Cr$_{16-N}$Co$_N$ was chosen as a model system. For each $N$ between 0 and 16, we have considered all possible ways of distributing the $N$ Co atoms among the 16$c$ site of the unit cell. First-principles total-energy calculations were then performed only for the symmetrically inequivalent configurations. In a similar way, we calculated the total-energies for C14 Nb(Cr$_{1-x}$Co$_x$)$_2$ based on Nb$_8$Cr$_{16-N}$Co$_N$. The same unit cell content as for the C15 phase was obtained by using 2$x$1x1 supercells. The $N$ Co atoms were distributed among the 2$a$ and 6$h$ sites of the hexagonal unit cell.

The Gibbs energy $\Delta G$ is given by:

$$\Delta G = \Delta H - T\Delta S$$  \hspace{1cm} (2)$$

The entropy for C15 and C14 Nb(Cr$_{1-x}$Co$_x$)$_2$ as disordered solution phases employing the ideal solution model is given by:

$$\Delta S = -R\left[x\cdot \ln(x) + (1-x)\cdot \ln(1-x)\right]$$ \hspace{1cm} (3)$$

The heat of formation $\Delta H$ was then calculated for the configuration with the lowest energy at each point $N$ from the total-energy of the compounds and the total-energy of the elements Nb, Cr and Co:

$$\Delta H = E_{Nb(Cr_{1-x}Co_x)_2} - E_{Nb} - (2-2x) \cdot E_{Cr} - 2x \cdot E_{Co}$$ \hspace{1cm} (4)$$

The Gibbs energy of the stable configurations of the C15 and the C14 structure at the composition N/16 with $N = 0$–16 are shown in Figure 2. The values are fitted with Redlich-Kister polynomials of 4th order:

$$\Delta G = ((x-1) \cdot \Delta G_{AB_2} + x \cdot \Delta G_{AB_2'}) + (x-x^2) \cdot [A + A(2x-1) + A(2x-1)^2 + A(2x-1)^3 + A(2x-1)^4]$$  \hspace{1cm} (5)$$

The phase boundaries associated with the first-order transition between the phases with C15 and C14 structure were located using the tangent construction.

The calculations predict in agreement with the experiment that NbCr$_2$ and NbCo$_2$ crystallize with the cubic C15 structure type. A small solubility of 2 at.% Co in C15 NbCr$_2$ is expected followed by a two-phase field up to 12 at.% Co. Due to the limited number of data points, the location of the two-phase field C14/C15 on the Co-rich side cannot be determined by the tangent construction. However, a small solubility for Cr in C15 NbCo$_2$ is expected from the data and a C14 phase Nb(Cr$_{1-x}$Co$_x$)$_2$ should form with a broad homogeneity range. The predictions are in good agreement with the experimental data as indicated by the top and bottom bars in Figure 2.

As a second example, the system TaV$_2$–TaFe$_2$ has been chosen to compare calculated with experimental data. No information for this system is available in the literature, except that TaV$_2$ and TaFe$_2$ crystallize with the C15 [7] and the C14 structure type [8], respectively. TaFe$_2$ is a paramagnet very close to a magnetic instability with strong ferromagnetic (FM) and antiferromagnetic (AFM) spin fluctuations [9]. Hence, one can expect that spin polarization plays an important role.

![Fig. 2: Gibbs energy of C15 and C14 Nb(Cr$_{1-x}$Co$_x$)$_2$. The solid lines are fits with Redlich-Kister polynomials. The top and bottom bars indicate the experimentally determined and the calculated width of the single phase fields of C15 and C14, respectively.](image-url)
However, due to the large number of structural/magnetic configurations spin polarization was not included in the current calculations.

The Gibbs energy of the stable configurations of the C15 and C14 phases are shown in Figure 3. The calculation predicts a solubility of Fe in TaV₂ up to 24 at.% and of V in C14 TaFe₂ up to 39 at.%. An additional phase change from C15 to C14 close to TaV₂ and the stability of C14 TaV₂ is expected from the calculated data. However, this is inconsistent with the experimental results. It is known that pseudo potential calculations tend to make wrong predictions in the case of Laves phases containing V [10]. If a full-potential code like FPLO is used [11], C15 TaV₂ is the stable polytype, in agreement with the experiments.

A series of Ta(V₁₋ₓFeₓ)₂ alloys with various Fe and V contents was prepared by arc-melting high purity elements as starting materials and performing a subsequent heat treatment at 1150 °C for 30 days. After the annealing, the samples were quenched in water. The composition of the samples was determined with ICP-OES. Metallographic examinations were carried out to check the phase content. The maximal solubility of Fe in TaV₂ at 1150 °C is 8 at.%, while the solubility of V in TaFe₂ is 43 at.%. In addition, a ternary Laves phase of the hexagonal C36 type has been observed with a small homogeneity range of 0.29 ≤ x ≤ 0.32. Figure 4 shows the experimental results of the phase analysis and the mean atomic volume plotted versus the composition x. As expected, the mean atomic volume decreases with increasing Fe content and the volume behaves according to Vegard’s volume rule. The calculated values are in good agreement with the experimental data, after the volume correction, except for the C15 phase close to TaV₂. The reasons for the deviation of the calculated mean atomic volume close to TaV₂ are yet unclear, but can be related to the wrongly predicted stability of C14 TaV₂.

Magnetism of Ta(V₁₋ₓFeₓ)₂

The change of the crystal structure is not the only interesting issue in Ta(V₁₋ₓFeₓ)₂. In the C14 phase, this system shows peculiar magnetic properties: In the range 0.75 ≤ x ≤ 0.95 it was reported to be an itinerant antiferromagnet, whereas for x > 0.95 the magnetic susceptibility of the system, measured with a magnetic field of 1T, did not show any phase transition but very high values for a band magnet, indicating the proximity of TaFe₂ to a FM instability [9]. In other words, TaFe₂ is considered to be paramagnetic (PM) with strong AFM and FM spin fluctuations. This statement is supported by the chemical and electronic similarity of TaFe₂ and NbFe₂, which has been investigated in our institute in detail [12-15]. By adjusting the precise composition within a narrow homogeneity range or by applying hydrostatic pressure, NbFe₂ can be tuned from ferromagnetism via an intermediate spin-density-wave (SDW) modulated state to a quantum critical point (QCP). Since the atomic volume of TaFe₂ is about 13.25 Å³ and thus slightly smaller than that of NbFe₂ (13.35 Å³) we expect TaFe₂ to be closer to the QCP than NbFe₂.
To get insight into the magnetic properties of Ta(V1–xFex)2 we have measured the temperature (T) and field (B) dependencies of the magnetization (M) of polycrystals with 0.7 ≤ x ≤ 1. The uniform susceptibility χ = M/B at B = 1 T is plotted in Figure 5 (upper panel) for selected samples and temperatures from 300 K to 2 K. The arrows mark the peak in χ at the Néel temperature TN, indicating a phase transition from a PM state into a low-T AFM state. At high and low V contents no phase transition is observed and the ground state is paramagnetic. However, there is a great difference between the values of the susceptibility for x = 0.7 (red line) and x = 0.98 (grey line) at 2 K. In the sample with x = 0.98 the susceptibility is enhanced by spin fluctuations by a factor of ~ 240 (Stoner factor) compared to the bare susceptibility estimated from band structure calculations. In NbFe2 this factor is ~ 180 [13]. This value confirms that the system at x ~ 1 is close to an FM instability. To know how large the fluctuating moment is in this sample, we have plotted χ–1 vs T in the lower panel of Figure 5 to analyze the Curie-Weiss behavior: The dashed line is a linear fit to the data yielding a fluctuating moment of 1.04 μB which is much larger than the induced magnetic moment of about 0.055 μB measured at 7 T (see Fig. 6). This is a common property observed in all itinerant magnets.

More evidence for the presence of the AFM state is given by the field dependent magnetization shown in Figure 6 for three PM samples and one AFM sample with x = 0.75. This sample shows an inflection point around 3 T emphasized in the inset where we have plotted the derivative dM/dB vs B. dM/dB shows a clear peak which shifts to lower fields with increasing temperature, as expected for an antiferromagnet.

From our susceptibility measurements with B = 1 T we have determined the magnetic phase diagram of Ta(V1–xFex)2 which is displayed in Figure 7. The red points indicate the Néel temperatures observed in our experiments, while the black ones have been extracted from Ref. [9], where the susceptibility has also been measured at 1 T. A clear AFM dome emerges in the PM phase of the diagram. There is a certain systematic discrepancy between these points, which is difficult to clarify. It could be explained by the fact that our V content
has been estimated by chemical analysis while the nominal one is given in Ref. [9]. However, if there is a systematic difference in $x$ we would expect our $T_N$ to be higher on one side and lower on the other side of the dome maximum. The overall behavior is consistent though.

**Conclusion**

The experimental determination of phase diagrams is a tedious, expensive and time consuming work because a large number of alloys have to be prepared, homogenized and characterized. Due to the ongoing improvements of theoretical methods like Density Functional Theory (DFT) and CALPHAD and due to the increasing amount of available computing power, brute force computations like the supercell approach become feasible, fast and cheap. In this work it has been shown that DFT computations in ternary Laves phases $A(B'_{1-x}B''_x)_2$ allow to make predictions about the phase stabilities, the unit cell geometry and the site occupation factors as a function of the composition. The computed values usually exhibit an offset but can be calibrated by a small number of experimental data.

The magnetic properties of the Ta(V$_{1-x}$Fe$_x$)$_2$ series basically agree with those found in literature and offer a great opportunity to study band-magnet quantum criticality in a stoichiometric compound at ambient pressure.

**References**


