Concentration dependence of the short-range order in the Ni-V and Pt-V systems

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The short-range order (SRO) in Pt-V and Ni-V systems has been studied by diffuse scattering of neutrons over a large concentration range. In both systems, a c-dependent SRO has been observed. We show that this concentration sensitivity has a different origin in the two cases. In Ni-V, the change of the SRO pattern is mainly due to c-dependent effective pair interactions (EPI), while in Pt-V, the EPI are c independent. We find explicit discrepancies between our results, deduced from measurements in the disordered state, and the electronic structure calculations, if they are performed in the ordered state. These discrepancies are due to the sensitivity of the electronic structure to the state of order.

I. INTRODUCTION

Short-range order (SRO) which appears in the high temperature disordered state of alloys has been extensively studied since the SRO topology reflects the underlying interactions of the system. We report on our measurements of the SRO in two different systems, Ni-V and Pt-V, undertaken to study the concentration dependence of effective interactions and to improve our general understanding of phase diagrams.

Several theoretical studies have been devoted to the concentration dependence of the SRO in binary alloys1,2 but few experimental works have been carried out with that perspective in mind. Experimentally, to our knowledge, the only system for which the SRO has been measured over a large concentration range is the Ni1−xCr system,3−5 where the SRO maxima are locked at the same positions for c = 1/4, 1/2, 3/4, and 5. In contrast, as we have shown in Refs. 6, 7, the topology of the SRO in the Pt-V system changes with the concentration. Despite those variations, inverse Monte Carlo simulations applied to the SRO lead to nearly c-independent effective pair interactions (EPI) from Pt3V to Pt8V. Furthermore, in order to check that this unexpected property cannot be extended to any alloy, the Ni-V system has been investigated since it looked very similar to the Pt-V system (platinum and nickel belong to the same column of the periodic table). The Ni-V and Pt-V systems display the same Pt3Mo,DO22, and A8B (Refs. 8, 9) ordered phases on the fcc lattice. However, although the phase diagrams are similar, the interactions should be different in the two systems since the SRO maxima are not located at the same positions: Pt3V displays maxima at the ⟨100⟩ positions while in Ni3V (Refs. 10, 11) the SRO maxima are located at the ⟨120⟩ q points.

II. EXPERIMENT

All the compounds studied in this paper were grown by the Czochralsky method. Their compositions were determined by electron microprobe. To within 1%, they were consistent with the expected stoichiometries, except for Pt8V which was found to contain 13.2% vanadium. This shift in concentration has been taken into account in the data reduction. The diffuse scattering of neutrons was performed on the spectrometer G44 at the laboratoire Léon Brillouin (CNRS/CEA), France. We followed the same procedure as outlined in Ref. 5. The ⟨100⟩ and ⟨110⟩ planes were explored in situ, with the incident wavelength λ = 2.59 Å. In order to reject the inelastic signal due to the high population of the phonon modes at high temperature, a time of flight analysis has been used. Under these conditions the energy resolution was never greater than 4 meV. After correcting for absorption, multiple scattering and Debye-Waller attenuation, the Warren Cowley parameters α(⟨nn⟩) = (⟨σσ⟩ − ⟨σ⟩)⟨σ⟩/4c(1 − c), and the size effect contribution were extracted from the diffuse intensity using a least square routine, based on a Sparks-Borie approach12 for displacements, up to the first order. The results are shown in Fig. 1.

III. CONCENTRATION DEPENDENCE OF THE SRO IN PT-V AND NI-V

A. Pt-V system

From Pt3V to Pt8V, we observe a large effect of the concentration on the SRO topology. As with Pd3V,11 the diffuse intensity of Pt3V is spread along the ⟨1k0⟩ direction with maxima at the ⟨100⟩ positions. These positions of the SRO maxima are not compatible with the DO22 ground state within the usual mean field approach. In Pt8V, the maxima are no longer located at special points of the fcc lattice. Instead, the ⟨100⟩ intensity is split along the ⟨100⟩ axis and presents a saddle point (see Fig. 1). We note that these maxima are no longer located just above the superstructures of the ordered state. The Bragg peaks of the A8B ground state are located at ⟨320⟩ and ⟨2240⟩ (and equivalent points), whereas the SRO intensity sits on an incommensurate q point, between ⟨000⟩ and ⟨100⟩. The Pt3V SRO displays a topology which is intermediate between Pt3V and Pt8V. As Pt3V, the maxima sit on the ⟨100⟩ points (and equivalent), but the broadening of the intensity profiles along the ⟨h00⟩ lines is reminiscent of the Pt8V splitting. A quite different topology has been measured in Pt3V. The SRO maxima are located at incommensurate positions along the ⟨1k0⟩ line. By symmetry, this leads to a hole at the ⟨110⟩ point. Other systems such as Cu3Zn,13 Cu3Au,14,15 Cu-Pd,16 or Cu-Al17 display a splitting in the same direction. In Sec. IV A, we comment about the link between the incommensurate maxima of the SRO and the real space dependence of the underlying interactions.
In the Ni-V system, from Ni$_2$V to Ni$_3$V, the intensity maxima are locked at the $(1\frac{1}{3}0)$ special points but, for Ni$_8$V, they suddenly shift to $(100)$. In Ni$_8$V, there is a broadening of the intensity profile along the $(h00)$ direction, but, within the limit of the experimental resolution, no splitting similar to Pt$_8$V has been observed. That SRO evolution is more pronounced than in Pt$_{1-c}V_c$ system, for which the maxima, even if they are $c$-dependent, are always located in the neighborhood of the $(100)$ $q$ point from $c = \frac{1}{7}$ to $c = \frac{2}{7}$.

FIG. 1. Experimental short-range order in the Pt-V and Ni-V systems; (100) plane.
Notice that, in contrast to Ni₃V, the dominant wave vector of LRO and those of SRO do not coincide anymore in Ni₈V, since the A₈B phase is built on a 2\^110 concentration wave.

IV. EFFECTIVE PAIR INTERACTIONS

We have interpreted the diffuse scattering using an Ising model that includes long range effective pair interactions, \( \sim E_{\text{PI}} \), up to the ninth neighbors \( \sum_{nm} V_{nm} \sigma_n \sigma_m + h \Sigma_n \sigma_n \), where \( \sigma \) represents the occupation variable and \( h \) the chemical potential. These EPI are not determined from \textit{ab initio} calculations but from inverse statistical methods applied to the measured diffuse intensity maps. We have used different statistical approaches: a Monte Carlo method, the gamma expansion method (GEM) \cite{GEM}, and the cluster variation method in the \( Q \)-space (\( Q \)-CVM) \cite{Q-CVM}. We show in Fig. 2 the 16 first EPI obtained by the different methods and using the diffuse intensity of Pt₃V. The agreement is excellent. We would like to stress that those three methods are based on quite different approaches and assumptions. The GEM is an analytical method, the \( Q \)-CVM is a mean field approach (quasianalytical), whereas the inverse Monte Carlo is a purely numerical technique.

A set of EPI has been obtained for each of the diffuse maps of the Fig. 1 using inverse Monte Carlo simulations. The interactions are displayed on Fig. 3.

A. Concentration dependence of the EPI in Pt-V

Despite the obvious topological changes of the intensity maps, the EPI’s of the Pt-V system do not depend much on concentration, except \( V_1 \). This behavior was unexpected, as any electronic calculation must take into account the band filling, which must induce changes of the EPI. We already noticed a similarly unexpected behavior for the Ni-Cr system.\(^5\) This weak \( c \) dependence of the interactions is confirmed by direct Monte Carlo simulations.

A single set of interactions correctly reproduces the \( c \) behavior of the SRO, from the incommensurate splitting along the \( \langle 1k0 \rangle \) direction in Pt₃V to the splitting along the \( \langle h00 \rangle \) direction in Pt₅V (Fig. 4). That strong \( c \) variation of the SRO simulated from the same interactions clearly shows that the Krivoglaz-Clapp-Moss formula\(^{19}\) in insufficient. It is thus desirable to devise a simple analytical expression for \( a(q) \) which goes beyond the mean field KCM formula. Even though it is more accurate, the more elaborated cluster variation method is not a good candidate, as it does not provide a direct analytical link between the \( V(R) \)’s and the \( a(q) \). In the Appendix, we give a derivation of the simple analytical theory we used in our previous paper.\(^7\) As is needed, this theory goes beyond the KCM approach. It explains the above result, i.e., how a \( c \)-dependent incommensurate SRO can be obtained from a unique set of EPI.

We now comment briefly about the link between the incommensurate maxima of \( a(q) \) and the real space topology of the EPI. It is often believed that an incommensurate SRO...
is the signature of long range interactions. Indeed, long-range oscillating $V(R)$, as those due to Fermi surface nesting, lead almost inevitably to incommensurate locations of the $\alpha(\vec{q})$ maxima, which may vary continuously with concentration or temperature. This is probably the case of some Cu-based alloys. In our case, the $V(R)$ are indeed incommensurate, but they do not seem long ranged. More precisely, if we try to fit them with a law of the form $\cos(\vec{k} \cdot \vec{r})/r^n$, the best fit is obtained for $n = 3$, and fits with $n = 1$ or $n = 2$ are pretty bad. This seems to exclude Fermi surface nesting effects. In fact, incommensurate, or even long-range interactions are not prerequisites to get an incommensurate $\alpha(\vec{q})$. An adequate competition between the $V(R)$ is sufficient. For instance, in the simple case $V_1 = 100, V_2 = 8, V_3 = 2$, $V(\vec{q})$ exhibits a commensurate minimum at $\langle 1 0 0 \rangle$, whereas the $\alpha(\vec{q})$ maxima are incommensurate, and splitted around $\langle 1 1 0 \rangle$. On heating, they shift towards $\langle 1 1 0 \rangle$.

B. Concentration dependence of the EPI in Ni-V

As in the Pt-V system, the SRO pattern in the Ni-V system is sensitive to the concentration as well, but this concentration sensitivity has a different origin. Contrary to the Pt-V system, the EPI’s in Ni-V significantly depend on the concentration (see Fig. 3). For example, the sign of $V_2$ changes from Ni$_2$V to Ni$_8$V. The SRO variations in Ni-V are mainly due to $c$-dependent EPI. In the Ni-V system, it seems that we

FIG. 4. Simulated SRO in Pt-V by Monte Carlo simulation in (a) Pt$_5$V, (b) Pt$_7$V, and (c) Pt$_9$V, in the (100) plane. For those simulations, we used the same EPI set obtained by inverse Monte Carlo simulation from the SRO of Pt$_3$V.
TABLE I. Ground states and transition temperatures calculated from EPI determined in the disordered phase of the alloy in the Pt-V and Ni-V systems. We note that, for Pt, the predicted ground state [phase 22 in the Kanamori nomenclature (Ref. 22)] differs from the observed one (the PtMo-like phase), but the calculated energy difference is very small (~9 meV).

<table>
<thead>
<tr>
<th>System</th>
<th>Ground state</th>
<th>Experimental ground state</th>
<th>and calculated</th>
<th>Experimental ground state</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt$_{1-c}$V$_c$</td>
<td>$c = \frac{1}{3}$</td>
<td>$A_4B$</td>
<td>$T_c^{\text{cal}} \approx 850$ K</td>
<td>$T_c^{\text{exp}} \approx 1090$ K</td>
</tr>
<tr>
<td>Ni$_{1-c}$V$_c$</td>
<td>$c = \frac{1}{3}$</td>
<td>$A_4B$</td>
<td>$T_c^{\text{cal}} \approx 500$ K</td>
<td>$T_c^{\text{exp}} \approx 678$ K</td>
</tr>
<tr>
<td>Pt$_2$Mo</td>
<td>$c = \frac{1}{3}$</td>
<td>$A_4B$</td>
<td>$T_c^{\text{cal}} \approx 1113$ K</td>
<td>$T_c^{\text{exp}} \approx 1318$ K</td>
</tr>
</tbody>
</table>

C. Properties deduced from the EPI

We display in Table I the ground states obtained with our sets of interactions and the corresponding transition temperatures, as calculated by Monte Carlo simulations. Except for the $A_4B$ stoichiometry, we obtain an overall agreement with the experimental data. In particular, the fact that, for Ni$_8$V and Pt$_8$V, we find the correct ground states is a strong indication of the long-range part of our interaction sets. Indeed, with only four interactions, the ground state at composition $c = \frac{1}{3}$ is degenerate among many $A_4B$ structures.

We note that, for Pt$_2$V, the ground state is predicted to be DO$_{23}$ instead of the experimentally observed DO$_{22}$ phase. However, the calculated energy difference between DO$_{23}$ and DO$_{22}$ is very small (~3.3 meV per site). More generally, we find that all the $L_12$-based long period structures are almost degenerate with DO$_{23}$. This is in agreement with the experimental observation of these long period structures in the pseudobinary alloys PtV-(Ti,Rh).

V. DISCUSSION

However, this qualitative agreement goes together with a quantitative discrepancy with electronic structure calculations (LMTO). The latter, based on ordered structures, lead to $\Delta E(L_12 - \text{DO}_{23}) = 65$ meV, whereas we find only 2 meV by our method, which relies on measurements in the disordered state. For Ni$_2$V, we already pointed out the same type of discrepancy between our approach based on the experiment and ab initio calculations. It had been suggested that this discrepancy could be partially attributed to electronic excitations. However, as the Sommerfeld approximation was used, this effect was overestimated. Since, Wolverton and Zunger have performed a more accurate calculation, showing that the first principles $\Delta E$, which is around 100 meV at $T=0K$, decreases only by 27% at 1400 K if the electronic and magnetic excitations are taken into account. Phonon excitation can also be suspected to explain that discrepancy, but, for Pd$_3$V, which is very similar to our compounds, Van de Walle et al. have estimated a phonon entropy difference to 0.08 $K_B$ atom, which corresponds only to a free energy difference of 10 meV at the temperature of our diffuse scattering measurements, i.e., 1400 K. Other more complicated effects cannot be completely excluded, but the simplest explanation is to assume that the EPI are sensitive to the degree of order, through an obvious blurring of the density of states (DOS) upon disordering. This effect is expected to be particularly important for the $L1_2$ structure of our alloys, which shows a strong DOS peak at the Fermi level, in both ferromagnetic and nonmagnetic states. A KKR-CPA calculation has been performed by Johnson on Ni$_3$V. For the fully ordered state of Ni$_3$V, he recovers the $\Delta E$ value obtained by LMTO but, in the disordered state, $\Delta E$ is found to be close to the values we deduced from our measurements. These facts are strong indications of the validity of his method.

The simulated values of the transition temperatures are generally about 200 K below the experimental values, except for Ni$_2$V and Pt$_2$V. For the latter compounds, the experimental $T_c$'s are at least twice the simulated ones (see Table I). The same kind of discrepancy has already been encountered in Ni$_3$Cr. This could be directly linked to the particular structure of the ground state found in these three $A_2B$ compounds. Their common “Pt$_{2-Mo}”$ ordered structure is built on a periodic stacking of pure (110) planes, two of $A$ atoms followed by one of $B$ atoms. That strong local inhomogeneity, which is very different from the disordered state, could explain why it is difficult to reproduce properties of the ordered state from EPI determined in the disordered phase. Calculations analogous to those performed by Johnson on Ni$_3$V should probably solve this problem.

VI. CONCLUSION

To conclude, for the Pt-V system, we found $c$-independent EPI, despite drastic changes of the SRO topology with concentration. We found the same $c$ independence of the EPI for the Ni-Cr system. This situation contradicts elementary arguments of electronic structure. The Ni-V system is less paradoxical to that extent. On the other hand, together with a qualitative agreement, we found quantitative
discrepancies between properties deduced from our measurements in the disordered state, and the electronic structure calculations, if performed in the ordered state. These discrepancies are most probably due to the local order dependence of the EPI. They are likely to be solved by calculations which are able to handle the degree of order, like the KKR-CPA calculations.

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APPENDIX

As explained above, we need a simple and direct expression of \( \alpha(\vec{q}) \), as a function of the \( V(\vec{R}) \)'s, that goes beyond the KCM formula. We present below a very simple derivation of such an expression.

The usual mean field theory, on which the KCM formula relies, is based on the equation

\[
\langle \sigma_n \rangle = \tanh \left( \beta \left( h_n - \sum_{p \neq n} V_{np} \langle \sigma_p \rangle \right) \right),
\]

where \( \beta = (kT)^{-1} \) and \( h_n \) is the local field applied at site \( n \). In this framework, the estimate of the susceptibility \( \chi_{mn} \) \( \equiv \partial \langle \sigma_m \rangle / \partial h_n \) includes not only the influence of \( h_m \) on \( \langle \sigma_n \rangle \), which is mediated through the lattice by any sequence of sites \( (p,q, \ldots) \) which link, via the interactions \( V_{pq} \), the site \( n \) and \( m \), but also the effect of this prior modification of \( \langle \sigma_n \rangle \) on all the sites \( p \neq n \). The change of magnetization on these sites induce an unwanted variation on \( \langle \sigma_n \rangle \). The way to get rid of this stray effect is to compute the effective field at site \( p(p \neq n) \) in the assumption that there is no spin on site \( n \), or, equivalently, to apply to each \( \langle \sigma_p \rangle \) a correction which annihilates the unwanted effect of \( \langle \sigma_n \rangle \). In the spirit of a high-temperature expansion, the correction, which must be subtracted, is the local susceptibility at site \( p \): \( \partial \langle \sigma_p \rangle / \partial h_p \), multiplied by the contribution of \( \langle \sigma_n \rangle \) to the molecular field at \( p \), i.e., \( -V_{np} \langle \sigma_n \rangle \). Contrary to the Onsager cavity approach, this correction is applied prior to the use of the fluctuation-dissipation theorem. Once corrected, Eqn. (A1) becomes

\[
\langle \sigma_n \rangle = \tanh \beta \left( h_n - \sum_{p \neq n} V_{np} [\langle \sigma_p \rangle + \beta (1-\langle \sigma_p \rangle^2) V_{np} \langle \sigma_n \rangle] \right).
\]

(A2)

Using the fluctuation-dissipation theorem on Eq. (A2), we obtain, in the Fourier space and for the disordered state

\[
\alpha(\vec{q}) = \frac{1}{1 + \Lambda + 4\beta c(1-c)V(\vec{q})},
\]

(A3)

where \( V(\vec{q}) \) is the Fourier transform of \( V(\vec{R}) \) defined by

\[
V(\vec{R}) = V(\vec{R}) \{1 - 2(1 - 2c)^2 \beta V(\vec{R})\}
\]

(A4)

with

\[
\Lambda = 16\beta^2 c^2 (1-c)^2 \sum \{V^2(\vec{R})\}.
\]

(A5)

Equation (A4) shows that the interaction \( V(\vec{R}) \), if positive, is more attenuated when \( V(\vec{R}) \) itself is large, when the temperature is low, and when the concentration is far from \( c = \frac{1}{2} \).

The more important feature of the above results is that they lead to a simple and direct expression for \( \alpha(\vec{q}) \). Analytical expressions of \( \alpha(\vec{q}) \) are also obtained within the gamma expansion method, the ring approximation, or the alpha expansion method, but these expressions are not direct, as they contain a parameter (the diagonal part of the self-energy), which must be determined self-consistently by requiring that the sum rule \( \Sigma_{\vec{q}} \alpha(\vec{q}) = N \) be fulfilled. Meanwhile, it is easy to show that the present expression of \( \alpha(\vec{q}) \) is equivalent, up to the second order in \( 1/T \), to the ring approximation. Finally, we note that the same expression of \( \alpha(\vec{q}) \) has been obtained independently by Tsatskis through a more formal and systematic high-temperature expansion.

The above expressions (A3)–(A5) for \( \alpha(\vec{q}) \) easily explain the \( c \)-behavior of the SRO topology. In the Pt-V case, the scaling of Eq. (A4) will mainly reduce the strongest interactions, i.e., \( V_1 \), and this for the lowest vanadium concentrations. The SRO will be then dominated by further EPI and will in general be incommensurate. That is the case in Pt5V, where the diffuse maxima appear at incommensurate positions along the \( \langle h00 \rangle \) line.

On the other hand, for higher vanadium concentration, the renormalization of \( V_1 \) will be negligible. The dominance of \( V_1 \) will yield, at high temperature, a standard KCM behavior, i.e., a large intensity ridge \( \alpha(\vec{q}) \) along the \( \langle 1k0 \rangle \). The exact position of the maximum along that ridge is dictated by the interactions \( V(i);i \approx 2 \). That is the case of Pt5V where a flat diffuse intensity is measured along the \( \langle 1k0 \rangle \) with small maxima in the same direction (Fig. 1). At lower temperatures, the intensity on \( \langle 100 \rangle \) should increase much faster that on other points and this should lead to a shift of the maximum along the \( \langle 1k0 \rangle \) line, towards the \( 100 \) point.7


M. Barrachin, A. Finel, R. Caudron, A. Pasturel, and A. Francois,
18 Magnetic SRO could not influence the diffuse intensity at the experimental temperature ($T=774$ K) since Ni$_3$V becomes paramagnetic at 10 K if we extrapolate the existing data (see Ref. 9).