

Long-Range Order and Short-Range Order in Pd₃V: Breakdown of the Mean-Field Theory

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Diffuse scattering experiments of electrons, neutrons, and x rays have been performed on Pd₃V. They all give rise to intensity maxima at positions (100), which indicates a local order different from that of the low-temperature D0₂₂ ordered phase, characterized by (1 $\frac{1}{2}$ 0) diffraction spots. This contradicts the predictions of the usual mean-field theory. By use of the cluster variation method (octahedron-tetrahedron approximation) it is shown that this surprising effect can be explained in a model with first- and second-neighbor interactions V_1, V_2 , of the same sign, with $V_2/V_1 \ll 1$.

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The simplest theory that describes order-disorder phenomena in binary alloys is the Bragg-Williams mean-field theory, but it is known to be quantitatively inaccurate. It can even be qualitatively wrong when dealing with ordering effects on the fcc lattice. Although there is still some controversy on the precise shape of the phase diagram in the case of first-neighbor interactions only, recent calculations based on the cluster variation method (CVM) or on Monte Carlo simulations¹ yield results quite different from those deduced from the mean-field theory.²

The mean-field Krivoglaz-Clapp-Moss (KCM) formula³ is generally used to describe short-range order and yields the most important concentration fluctuations. In the case of short-range pair interactions, the q vectors of the concentration waves are limited to so-called special points.⁴ At low temperature, according to the mean-field theory, the ordered phases are generally driven by the same kind of concentration waves. However, it is not always possible to build such phases. In the fcc system, there is a family of A_4B alloys (Ni₄Mo, Au₄Cr, etc.) of the (1 $\frac{1}{2}$ 0) type, whose ordered state ($D1_a$ type) is not described by (1 $\frac{1}{2}$ 0) waves but by the related ones $\frac{1}{2}$ (420).⁵ This is not inconsistent with the mean-field theory since there is no way to build any ordered structure at this stoichiometry with (1 $\frac{1}{2}$ 0) waves. At the A_3B concentration, on the other hand, there are ordered states corresponding to both special points (100) and (1 $\frac{1}{2}$ 0) ($L1_2$ and D0₂₂, respectively). However, we present here results on Pd₃V for which short-range order is of (100) type whereas the ordered phase is D0₂₂. This is in complete contradiction with the usual mean-field theory. We show that this surprising change in local order from short-range order (SRO) to long-range order (LRO) can be understood by use of tetrahedron-octahedron CVM calculations.

The Pd-V phase diagram displays several ordered structures on the fcc lattice and a large domain of existence of the disordered phase. The atom size disparity is small and there is no magnetism (which remains to be understood).⁶ These properties make Pd₃V a very suit-

able system for a detailed study of order phenomena. Pd₃V orders according to the D0₂₂ structure below $T=825^\circ\text{C}$ and melts at 1400°C . We have performed neutron and x-ray diffuse scattering experiments on single crystals to determine the SRO-induced intensity. The neutron experiments have been made at the reactor Orphée (Laboratoire Léon Brillouin-Commissariat à l'Energie Atomique, Saclay) on a 64-detector spectrometer with a wavelength $\lambda=2.6\text{ \AA}$. The sample is in a furnace and a time-of-flight analysis allows selection of the elastic part of the signal. The required corrections (background, Debye-Waller, static displacements⁷) have been performed. The diffuse intensity has been measured in the (100) plane at $T=840$ and 940°C (Fig. 1). The x-ray experiments have been carried out at the Laboratoire pour l'Utilisation du Rayonnement Electromagnétique (LURE, Orsay) on a four-circle spectrometer,⁸ in collaboration with S. Lefebvre and M. Bessière. The sample was annealed at $T=840^\circ\text{C}$ and oil quenched. The diffuse intensity has been measured in the whole minimum volume, and Fig. 2 shows the results in the (100) plane. Details will be given elsewhere. In both experiments, the diffuse intensity concentrates on $[1\zeta^*0]$ lines with clear maxima at (100) points. Electron-diffraction observations on quenched samples are also in agreement with these results (Fig. 3). Thus the short-range order is of the (100) type instead of the expected (1 $\frac{1}{2}$ 0) one.

The mean-field theory relates through the KCM formula, $\alpha(q)=[1+4c(1-c)V(q)/kT]^{-1}$,³ the Fourier transform of the pair interaction, $V(q)$, to the Fourier transform of the Warren-Cowley SRO parameters, $\alpha(q)$. The diffuse intensity $I(q)$ is proportional to $\alpha(q)$. $I(q)$ is then maximum when $V(q)$ is minimum and the position of this maximum does not depend on temperature. To stabilize D0₂₂ as a ground state, at least first- and second-neighbor interactions V_1, V_2 are necessary, with $V_1 > 0$, $V_1/2 > V_2 > 0$.^{3,9} According to the mean-field theory, this regime of V_1, V_2 gives rise to a maximum of diffuse intensity at (1 $\frac{1}{2}$ 0) points, whereas it is at (100) points when $V_2 < 0$, $L1_2$ being then the ordered phase

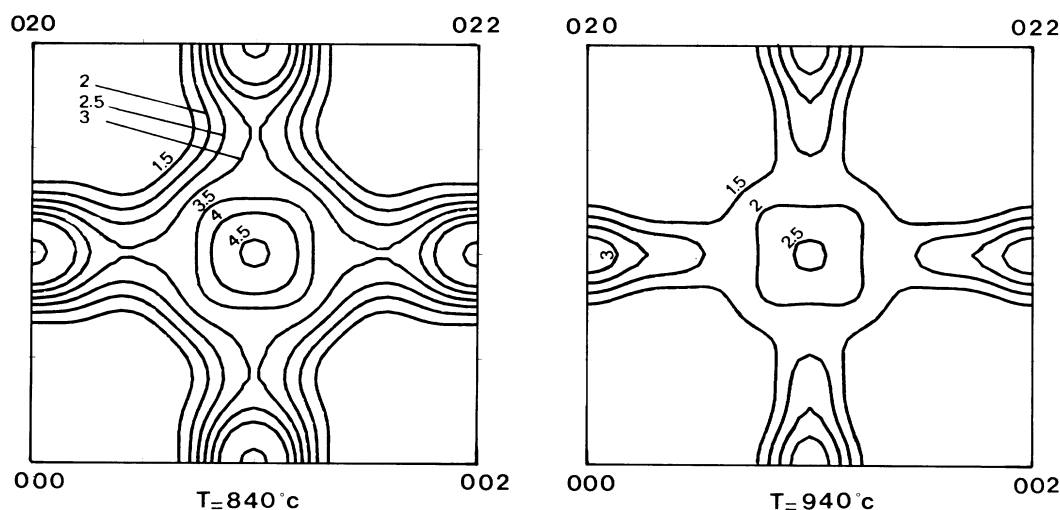


FIG. 1. Neutron diffuse scattering intensity (Laue units) in the (100) plane for a Pd_3V single crystal at $T=840^\circ\text{C}$ and $T=940^\circ\text{C}$.

(Fig. 4). Obviously, we need a better thermodynamic theory to account for the SRO in Pd_3V .

We have then undertaken detailed CVM calculations in the tetrahedron-octahedron approximation to investigate in particular the regime $V_1, V_2 > 0$ with $0 < V_2/V_1 \ll 1$. The corresponding phase diagram (Fig. 5) needs some comments: Whereas the mean-field theory predicts that the $V_2=0$ line separates $D0_{22}$ from $L1_2$ at any temperature (Fig. 4), our CVM results indicate a narrow regime where $L1_2$ is stabilized by entropy effects on the $D0_{22}$ side ($0 < V_2/V_1 < 3 \times 10^{-3}$). This is consistent with arguments based on a low-temperature expansion.^{10,11} The critical order-disorder temperatures are expected to be quite accurate (when $V_2=0$, it is only 1% above the Monte Carlo estimates).¹ The transition is

strongly of first order, the two order parameters necessary to describe the $D0_{22}$ structure being larger than 0.8 at the transition.

We have then calculated $\alpha(q)$ in the disordered state by using the appropriate Sanchez's extension of the KCM formula.¹² A first remarkable result is that $\alpha(q)$ is no longer constant on the $[1\bar{1}0]$ lines when $V_2=0$. Instead $\alpha(q)$ is maximum at the (100) points which is consistent with high-temperature series expansion by Ferer and Wortis¹³ {the tetrahedron CVM also yields a constant $\alpha(q)$ along $[1\bar{1}0]$ lines}. When V_2 is positive, the position of the maximum depends on temperature: At high temperature the maximum is at $(1\frac{1}{2}0)$ (the mean-field theory is asymptotically exact when $T \rightarrow \infty$) but at lower temperature, when V_2/V_1 is small enough, $\alpha(q)$ is maximum at (100) (Fig. 6). Note that in the regime $V_2 > 0$, the domain of $\langle 100 \rangle$ instability ($0 < V_2/V_1 < 8 \times 10^{-2}$) is much larger than the $L1_2$ one.

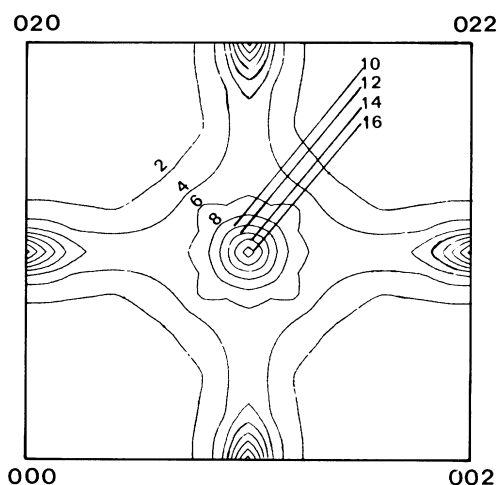


FIG. 2. X-ray diffuse scattering intensity (arbitrary units) in the (100) plane for a Pd_3V single crystal oil quenched from $T=840^\circ\text{C}$.

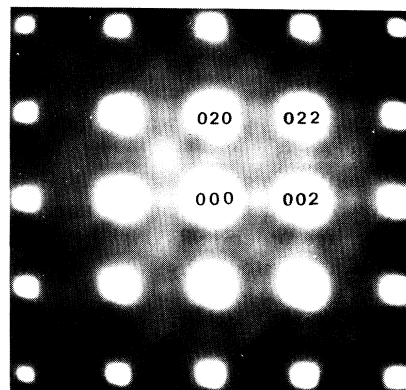


FIG. 3. Electron-microscopy (100) diffraction pattern on a Pd_3V sample oil quenched at $T=840^\circ\text{C}$.

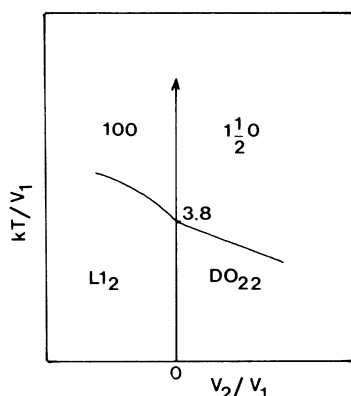


FIG. 4. fcc phase diagram in the mean-field theory for A_3B alloys.

These calculations show evidently that it is possible to have SRO of $\langle 100 \rangle$ type above DO_{22} as observed in Pd_3V . Monte Carlo simulations have confirmed our results.¹⁴ Note also that a completely similar theoretical phase diagram would be obtained for equiconcentrational alloys with $L1_2$ replaced by $L1_0$ and DO_{22} by A_2B_2 ($LiFeO_2$ -type),¹¹ but to our knowledge the A_2B_2 structure has not been observed in binary metallic alloys.

This unexpected behavior is basically related to the quasidegeneracy of the system when V_2 is small. When $V_2=0$, all structures built on $L1_2$ by introduction of conservative antiphase boundaries perpendicular to a $\langle 100 \rangle$ direction have the same ground-state energy, DO_{22} being

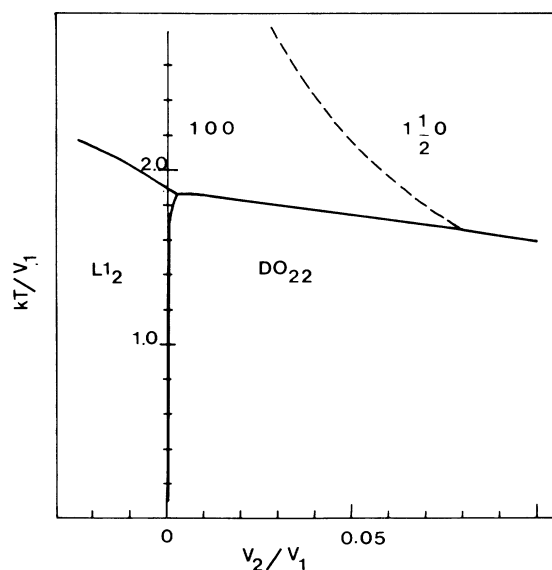


FIG. 5. fcc phase diagram in the tetrahedron-octahedron CVM approximation, at constant chemical potential which corresponds to an almost temperature-independent concentration $c = 0.27 \pm 0.01$.

the simplest of these structures. All of them give rise to superstructure spots located on the $[1\bar{1}0]$ lines. In the disordered state, according to the mean-field theory, when the interactions are short ranged, the intensity is almost entirely concentrated on these lines and constant along them. Our calculations indicate that entropy effects lift this degeneracy in favor of $\langle 100 \rangle$ -type ordering. Such effects are reminiscent of those observed in the axial next-nearest-neighbor Ising model, but notice that here low-temperature expansions indicate that long-period structures are not stabilized between $L1_2$ and DO_{22} ^{10,11}; branching processes, however, might occur at finite temperature and are currently under study.

The experimental results on Pd_3V are thus qualitatively well explained by use of only first- and second-neighbor interactions. This is consistent with recent calculations showing that, in transition-metal alloys, the ordering pair interactions should be short ranged.¹⁵ In fact, these electronic structure calculations predict that interactions up to fourth neighbors are relevant. A detailed interpretation of our data will then require, in the future, inclusion of interactions up to V_4 , but it is already clear that the parameter playing the part of V_2 will then be the antiphase energy $\xi = V_2 - 4V_3 + 4V_4$ which should be much smaller than V_1 for Pd_3V . Detailed electronic structure calculations are in progress to calculate these quantities.¹⁶

To summarize, we have shown that in fcc A_3B alloys with predominant first-neighbor interactions, the local order in the disordered phase (SRO) can be different from that of the low-temperature ordered phase. This is related to the quasidegeneracy of the system and to the strong first-order character of the order-disorder transi-

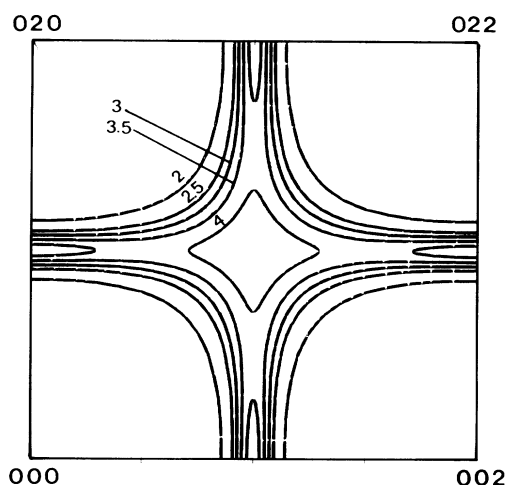


FIG. 6. $\alpha(q)$ (Laue units) in the tetrahedron-octahedron CVM approximation, $kT = 2V_1$, $V_2/V_1 = 0.05$, and $c = 0.27 \pm 0.01$.

tion. This effect has been measured in Pd_3V , but electron microscopy experiments indicate that it also occurs in Pt_3V .¹⁷ It should be observed in similar systems such as Ni_3V . It does not occur usually in other degenerate systems presenting long-period structures such as Au_3C , Cu_3Pd , Ag_3Mg ,^{18,19} In these cases the short-range order mimics the long-range order, which suggests that in these systems interactions beyond fourth neighbors should be taken into account.

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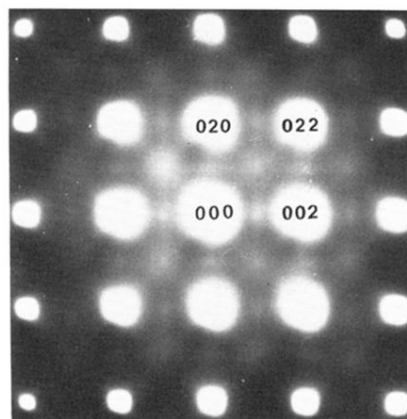


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