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Al₃Ti alloy: long-period states and electronic structure

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Abstract

On the basis of *ab initio* calculations of the electronic structure and electronic susceptibility $\chi(\vec{q})$, the relations between the nesting properties of the Fermi surface and the features of long-period structures in an Al₃Ti alloy are studied. The observed dependence of the long period $2M$ on temperature is analysed.

It is a matter of general knowledge that in the systems Cu–Au, Cu_{3–x}Pd_{1+x}, Cu_{3–x}Pt_{1+x}, Ag_{3–x}Mg_{1+x}, etc, quite extraordinary ordered phases—long-period superstructures (LPSs)—occur [1–7]. In one-dimensional LPSs (which are most often formed) the long period is oriented along the [100] direction. The length of the period $2M$ is controlled by the linear density of antiphase boundaries (APBs), i.e., two- or quasi-two-dimensional flat defects, where the long-range order parameter changes the sign of its phase, this parameter corresponding to short-period superstructures L1₀ or L1₂ (the latter will be referred to as basic structures here).

In accordance with the current concepts, the formation of an LPS is associated with the Peierls instability of the electron spectrum $\varepsilon_\lambda(\vec{k})$, conditioned by the presence of flat (nesting) patches on the Fermi surface (FS) separated by vector $2\vec{k}_F$. Disappearance of the instability consists in the formation of an LPS with the period $2M = \pi/|\vec{k}_F|$ accompanied by the opening of the energy gap in the electron spectrum over the entire area of such patches. Due to this, the excess in energy appears to be sufficiently large (with respect to their area) to destabilize the crystal structure [8–14] or to ensure a tendency to the formation of a long period in the system.

Long-period structures occur not only in alloys based on noble metals but also in other systems, particularly in such alloys as Al_{3–x}Ti_{1+x}. In their features they are similar to the structures formed in Ag_{3–x}Mg_{1+x} alloys. They possess a relatively short period compared to LPSs in Cu–Au alloys, they are stable within the entire temperature interval, and are strictly regular, ordered mixtures of domains with different lengths. Note that the period $2M$ is invariably commensurate with respect to the basic superstructure L1₂, and the average period is expressed as a rational fraction m/n (where m and n are integers) [15].

It is, however, to be noted that in many respects the Al_{3–x}Ti_{1+x} system is unique. Unlike the alloys based on noble metals, it maintains its ordering at relatively high temperatures,

acting in fact as an intermetallic compound rather than an alloy. When the composition or temperature are varied, the values of m/n are changed in a discrete fashion (the so-called ‘devil’s staircase’ of commensurate transitions is realized), with the range of these m/n variations being anomalously wide. For instance, in $\text{Al}_{72}\text{Ti}_{28}$, the m/n ratio grows from 1.33 to 1.77 for temperature increasing from 700 to 1200 °C [15].

A typical feature of long-period structures in the alloys in question is the fact that their stabilization cannot be interpreted in terms of considerations of decreasing electron energy. Indeed, these structures occur in the temperature interval bounded from above by a low-symmetry ordered phase L1_2 with a short period, and from below by a D0_{22} phase. Under these conditions, the L1_2 phase should be inferior to the D0_{22} phase in energy, and its thermodynamic advantage at higher temperatures can be achieved by higher entropy only. Earlier, this circumstance provoked to some scepticism regarding whether it is expedient to associate the transitions in LPSs with Peierls instability. In reality, as follows from [16], there is no conflict between the ‘energy’ and ‘entropy’ aspects of this problem. If we assume that the long-range character of ion interactions via the conductivity electrons gives a minimum in the Fourier-image ordering potential $V(\vec{q})$ at a certain random point $\vec{G} \pm 2\vec{k}_F$, then it appears that at very low energies the lowest system energy is achieved for a commensurate LPS with an average period which is very different from $M = (1/2)|\vec{G} \pm 2\vec{k}_F|$ (it is equally possible for a conventional short-period structure to possess the lowest energy). When the temperature is increased, the system undergoes a whole series of such transitions (‘devil’s staircase’), and the value of M approximates $(1/3)|\vec{G} \pm 2\vec{k}_F|$. Therefore, the long period predicted by the electronic theory should in fact correspond to high (!) rather than low temperatures.

In view of the above considerations, it is challenging to investigate whether the formation of LPSs in the $\text{Al}_{3-x}\text{Ti}_{1+x}$ system is associated with long-range interactions of electronic nature, i.e., with the presence of flat patches or ones coinciding in shape, capable of initiating the formation and stabilization of LPSs.

Since LPSs have a period that is a multiple of the lattice parameter of the basic L1_2 structure, we have to consider the electron spectrum of the Al_3Ti alloy ordered as the L1_2 type to be an initial spectrum, notwithstanding the fact that this structure has never been reported in it. We followed this approach in our early work to study the role of flat FS patches in the formation of 1D and 2D LPSs in the noble-metal alloys [16–20].

It is noteworthy that the major quantity in our approach is the susceptibility of non-interacting electrons $\chi(\vec{q})$ calculated using the electron energy spectrum of the alloy. Given the fact that on FS there are flat patches or ones coinciding in shape divided by the nesting vector $2\vec{k}_F$, then the function $\chi(\vec{q})$ would have a certain feature for the same vector (Kohn’s feature). Depending on the nesting ‘quality’ (i.e., the degree of similarity of overlapping patches), Kohn’s feature in the electronic susceptibility is a kink, a step, or even a peak. Note that the more pronounced the feature in $\chi(\vec{q})$, the higher the excess in energy achieved in the course of LPS formation.

The electron energy spectra were calculated by the full-potential LMTO method within an approximation of a local electron density [21]. The exchange–correlation potential was taken according to von Barth and Hedin [22], and the integration over the occupied states was performed using the tetrahedron method [23], with 126 reference points used in calculating the spectrum $\varepsilon_\lambda(\vec{k})$ and 4851 points in the irreducible part of the Brillouin zone (BZ) in calculating $\chi(\vec{q})$. The lattice parameter was taken to be 7.264 au for the D0_{22} structure with $c/a = 2.23$ [24]. When calculating the susceptibility of non-interacting electrons $\chi(\vec{q})$, we included only those energy bands that intersected the Fermi level and determined the behaviour of this parameter.

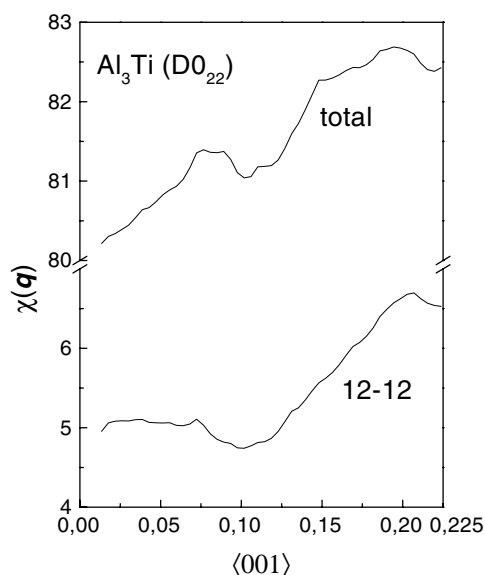


Figure 1. The electronic susceptibility $\chi(\vec{q})$ for the Al₃Ti system ordered as the D0₂₂ ($M = 1$) superstructure along the $\langle 100 \rangle$ direction (Γ -X). Also shown is the partial contribution from the intraband electronic transitions 12–12 (bottom curve).

Figure 1 shows the susceptibility $\chi(\vec{q})$ for the Al₃Ti system calculated in terms of the initial experimentally observed superstructure D0₂₂ ($M = 1$) along the $\langle 001 \rangle$ direction corresponding to the long period. A principal peculiarity of this curve is the maximum in $\chi(\vec{q})$ located in the vicinity of the BZ boundary and showing a tendency of this system to double its period along the direction under study. A structure superior to D0₂₂ would be D0₂₃ ($M = 2$), whose domains are observed to be mixed with the D0₂₂ domains in the cases of slight deviation from stoichiometry [15].

The reason for the above-mentioned maximum in $\chi(\vec{q})$ consists in the following. Three energy bands—the 12th, 13th, and 14th—intersect the Fermi level in Al₃Ti. An analysis, however, showed that it is just one partial contribution from the intraband electronic transitions 12–12 that virtually totally controls the behaviour pattern of $\chi(\vec{q})$ (figure 1). An analysis of the FS geometry proved that on the layers of the 12th band there are some cylindrical regions separated by the vector $\vec{q}_n = (\pi/c)\langle 001 \rangle$, where c is the respective lattice parameter. The \vec{q}_n -vector is clearly seen in the fragments of the FS cross-sections in two mutually orthogonal planes in figure 2.

However, the special features of the electron spectrum of the low-temperature D0₂₂ phase are incapable of accounting for the formation of LPSs with half-periods lying in the range from 1 to 2, i.e., those observed experimentally as the temperature was increased. There appears to be a need for calculating and analysing the electron spectrum of a hypothetical structure L1₂ whose elements constitute the LPS observed (the volume per atom should be the same as in D0₂₂).

Shown in figure 3 is the susceptibility $\chi(\vec{q})$ calculated for Al₃Ti ordered as the L1₂ structure along the $\langle 100 \rangle$ direction of the BZ. It is worth pointing out a local maximum at $|\vec{q}_n| = 0.35$ characterizing this system instability with respect to the formation of a long period with $M = 1.47$. An analysis of partial contributions to the total susceptibility $\chi(\vec{q})$ showed that this local maximum is caused entirely by the contribution from the intraband transitions 7–7

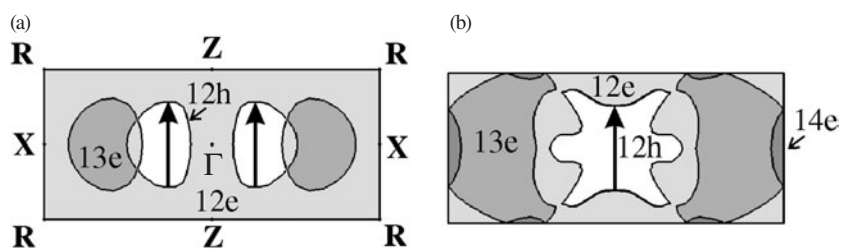


Figure 2. Fragments of the FS cross-sections in two mutually perpendicular planes: $z = 0$ (a), $x = 12.5(2\pi/a)$ (b). Arrows show the nesting vector.

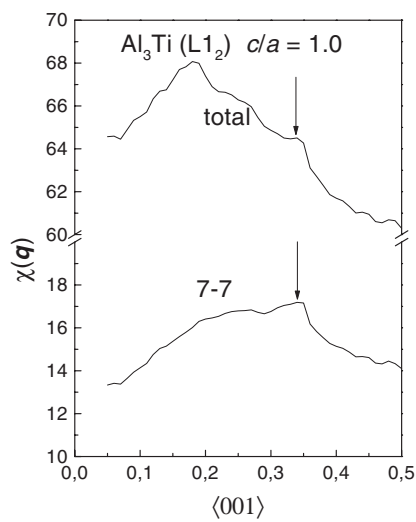


Figure 3. The electronic susceptibility $\chi(\vec{q})$ for the Al_3Ti system ordered as the $L1_2$ superstructure along the $\langle 001 \rangle$ direction. Also shown is the partial contribution from the intraband transitions 7-7 (bottom curve).

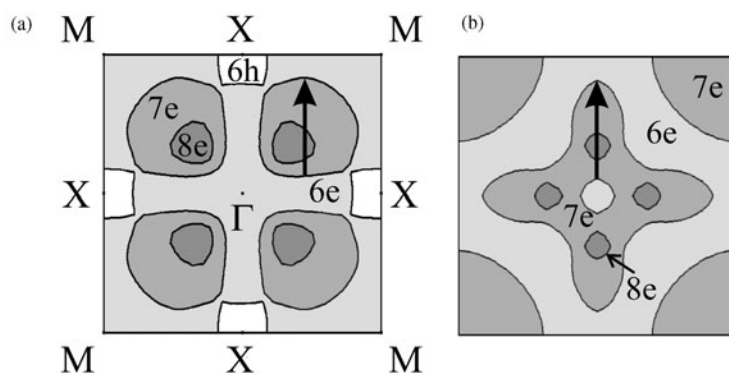


Figure 4. Fragments from the FS cross-sections in two mutually perpendicular planes: $z = 0$ (a), $y = 0.23(2\pi/a)$ (b). Arrows show the nesting vector.

plotted in figure 3. It is evident from the figure that at $|\vec{q}_n| = 0.35$ this contribution exhibits a well-pronounced maximum, which is indicative of the presence on the FS of overlapping

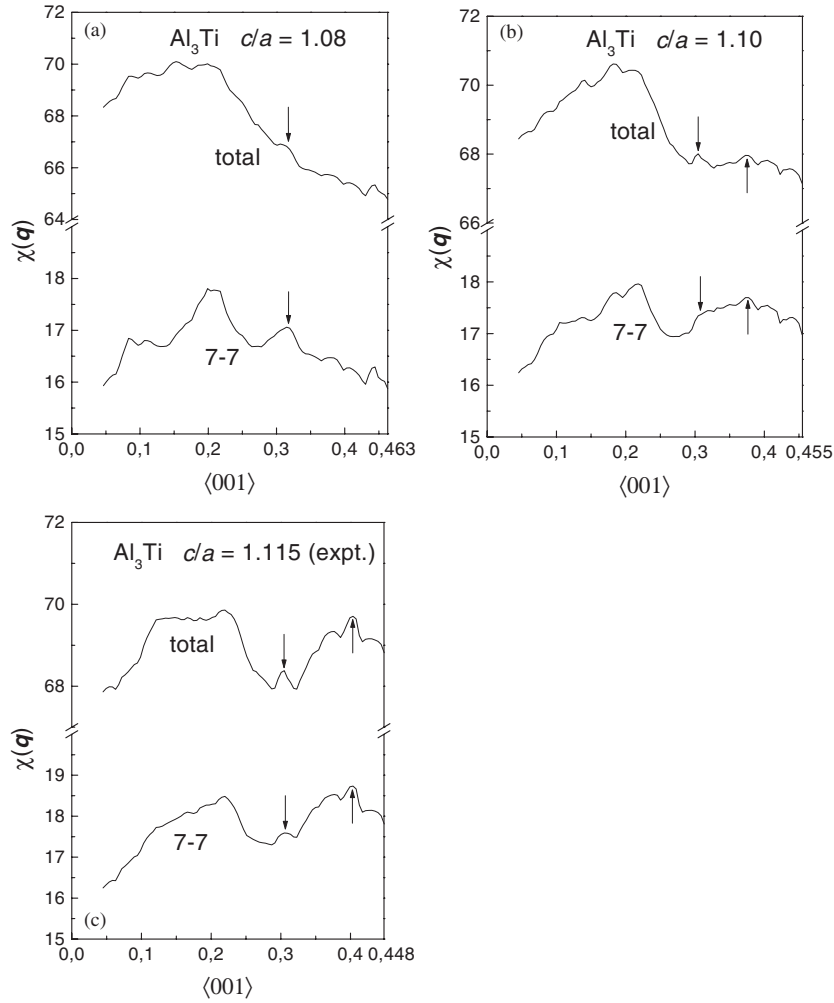


Figure 5. The electronic susceptibility $\chi(\vec{q})$ at different degrees of tetragonality: $c/a = 1.08$ (a), $c/a = 1.1$ (b), and $c/a = 1.115$ (c).

patches separated by the vector $\vec{q}_n = 0.35(2\pi/a)\langle 001 \rangle$. This vector is depicted in figure 4 on two mutually perpendicular FS cross-sections.

It should be emphasized that the low-temperature $D0_{22}$ structure possesses a quite high degree of tetragonality $c/a = 2.23$ [24]. It would, therefore, be reasonable to carry out the electron spectrum and susceptibility calculations for the $L1_2$ structure using the same tetragonality distortion as in $D0_{22}$, i.e., at $c/a = 1.115$. Here we should draw attention to the following circumstance: from general considerations, one may assume that the larger the value of a period is, the smaller the tetragonality of the primitive unit cells composing this structure should be. Hence, in the limit of an infinitely long period, this LPS might transform into a conventional cubic $L1_2$ structure. On the other hand, it is the simplest LPS formed in Al_3Ti (i.e., $D0_{22}$) that would display maximum tetragonality. Thus, to get a comprehensive understanding of the problem we should investigate the structures with intermediate degrees of tetragonality distortion also. In this work we have treated the Al_3Ti alloy as an $L1_2$ structure with the c/a parameter varied from 1 to 1.115.

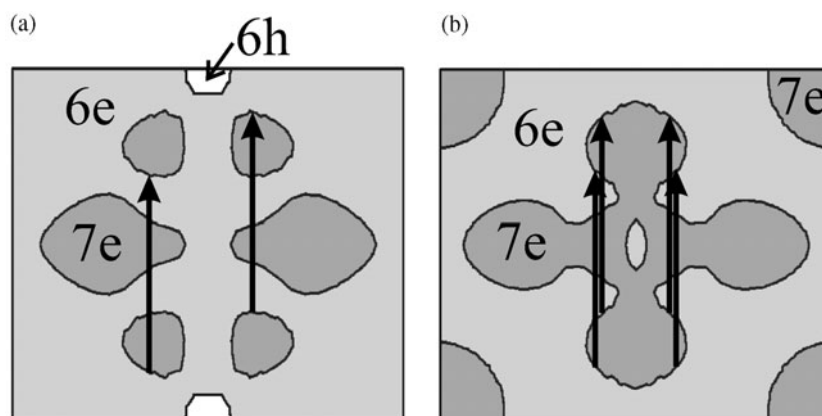


Figure 6. Fragments from the FS cross-sections at $c/a = 1.115$: $x = 0.1(2\pi/a)$ (a) and $y = 0.17(2\pi/a)$ (b).

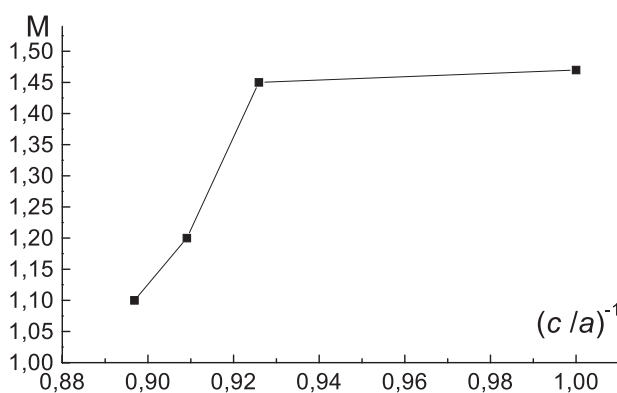


Figure 7. The dependence of the half-period of the LPS M on the reciprocal tetragonality parameter $(c/a)^{-1}$.

The curves $\chi(\vec{q})$ presented in figure 5 are the calculations for different c/a values. It is clear from the figure that the feature observed in a cubic $L1_2$ structure at $\vec{q}_n = 0.35(2\pi/a)\langle 001 \rangle$ (see figure 3) shifts to the right as the c/a value increases, and then gradually deteriorates. When $c/a = 1.10$, a new peculiarity is developed at $|\vec{q}_n| = 0.42(2\pi/a)$. Not only is this peculiarity shifted to the right, but also it becomes more marked. For the experimentally observed tetragonality, this feature corresponds to the vector of magnitude $|\vec{q}_n| = 0.46(2\pi/a)$, which conforms to the long period $M = 1.1$. All the vectors cited above could be matched with the respective overlapping FS patches divided by them. Depicted in figure 6 are the fragments of the FS cross-sections for $c/a = 1.115$ ($\vec{q}_n = 0.46(2\pi/a)\langle 001 \rangle$).

The results obtained can be summarized as a dependence of the length of the half-period M on the tetragonality parameter c/a of a primitive unit cell of $L1_2$ (figure 7). For the tetragonality used in the experiment, $M = 1.1$, which is very close to that in the low-temperature structure $D0_{22}$ ($M = 1$). As the tetragonality is decreased, the antiphase domain is seen to grow, and in a cubic structure, $M \approx 1.5$. Here the role of $(c/a)^{-1}$ could be that of temperature. The lower the tetragonality, the higher the temperature, and the longer the LPS period. These results can be qualitatively compared to the experimentally observed dependence of M on temperature [15].

Note that in [17] we reported that it is the long-range order parameter η that is responsible for the long period in Cu–Au systems, with the length of the LPS period changing with this parameter. The long-range order parameter also depended on temperature, decreasing as the temperature increased. In Al₃Ti, we observe a similar behaviour with the difference being in the degree of tetragonality distortion c/a rather than the order parameter.

To sum up, we may conclude that in the Al₃Ti alloy, as well as in other systems with LPSs, the electronic structure features, in particular the local FS geometry, play a significant (if not decisive) role in the formation and stabilization of long-period structures.

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