Nanogrooves generated on Au surfaces by low-temperature electron irradiation

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Abstract

The anisotropical nanogroove generation on the exit surface of Au(0$\bar{1}$1) foils by 400keV electron irradiation along the [001] and [0$\bar{1}$1] directions at 95 K is studied and compared with that obtained on Au(001) foils. Long or short grooves, with widths between about 1 and 2 nm, on the Au(0$\bar{1}$1) and Au(001) surfaces are found. They are characterized by the elongating direction of [100] and the dominant facets of (100) or (010), which are parallel to the incident beam. In some irradiated areas generation of grooves is observed to develop unevenly. The anisotropical groove growth mechanism is discussed in terms of anisotropical mass transport due to surface collision sequences.

1. Introduction

In the past intense convergent electron beams were utilized for nanometerscale etching, lithography and hole formation [1-3]. Recently, employing parallel electron beams of several hundreds of nanometers diameter, we have generated aligned nanogrooves and nanoholes on the exit surface of thin {001} gold foils [4] for the first time. The beam energies ranged from 360 keV, which is close to the threshold energy for the sputtering [5], to 1250 keV, which is somewhat higher than the critical energy of Frenkel pair production in the bulk material [6]. The irradiation temperature was about 100 K where surface vacancies are likely to be thermally immobile.

It was found that the anisotropy of nanogrooves depends on the irradiation direction and that nanoholes, which may reach depths of more than 20 nm, develop mainly along the beam direction. Moreover, the nanoholes are found to transform into voids of larger diameters at room temperature. The formation mechanism of these nanogrooves and nanoholes must be quite different from the convergent electron beam processing because the diameter of the electron beam used in our study is much larger than the size of nanoholes and nanogrooves. We have suggested that the aligned nanogrooves form by a self-organizing process controlled by collision sequences occurring on the surfaces. If so, the anisotropical groove formation should depend on the crystallographic plane of the foil surface.

The present paper compares the nature of nanogrooves generated between Au{001}- and Au{011}-oriented foil surfaces and discusses their growth process, taking account of the anisotropical mass transport under irradiation.

2. Experiments

A pure gold rod with nominal purity of 99.998% was cold rolled to thin foils with a thickness of about 100 μm. After annealing at 1200 K for about 2 h in order to eliminate defects, they were thinned by jet electropolishing. Grains with surface orientations near (001) or (0$\bar{1}$1) were selected and irradiated at 95 K with 400keV electrons in a JEOL-JEM4000FX electron microscope, equipped with a GATAN liquid nitrogen cooling stage. The irradiations were done along two different crystallographic directions near [001] and [0 $\bar{1}$1], using an electron beam diameter of typically some hundreds of nanometers on the foil surface. Though the surface orientation and observation direction are not strictly along the main crystallographic orientations, we will indicate the index hereafter. The electron microscopy observations were made under kinematic and slightly underfocus (so-called void contrast) conditions along different crystallographic directions and with strongly reduced beam currents in order to suppress additional sputtering.

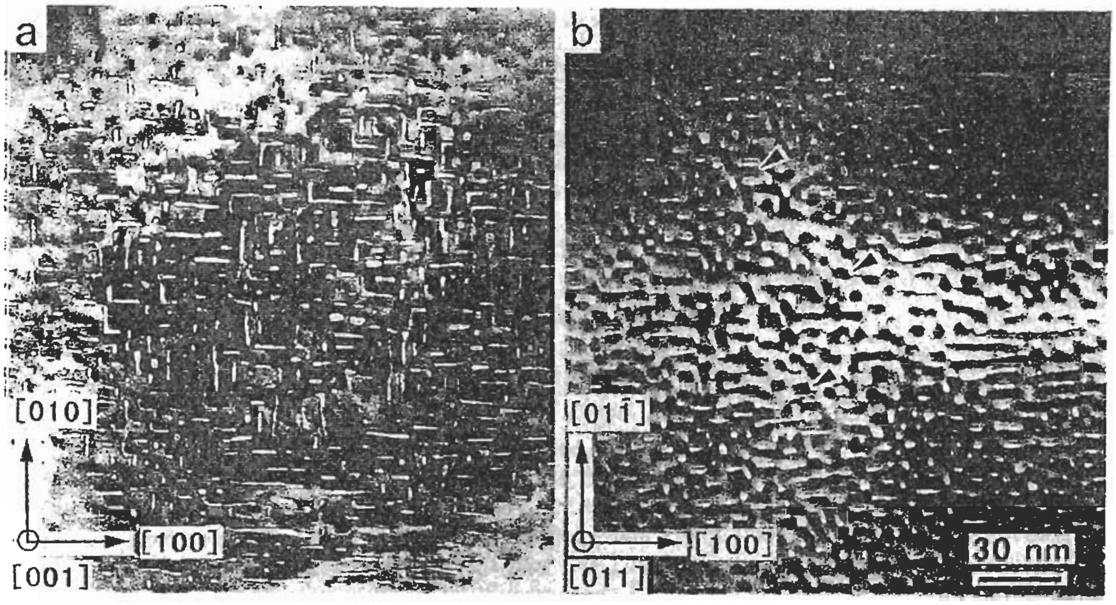

Fig. 1 Electron micrographs of an Au(001) foil irradiated along (a) [001] and (b) [011] with 400 keV electrons at 95 K. The photos are arranged to observe from the eroded surface side. Anisotropical growth of nanogrooves are seen with bright contrast. Short grooves elongating along $[01\bar{1}]$ can be seen in addition to long ones along [100] in photo (b). Circular dark areas which correspond to hillocks are denoted by arrows.

3. Results

Fig.1a shows a sputter eroded structure of a (001)-oriented foil after irradiation with 400keV electrons along [001] at 95 K. Areas with sharp bright contrasts with widths between 1 and 2 nm are seen. They are elongated almost linearly and uniformly along [100] and [010]. Stereomicroscopy revealed that the bright areas correspond to grooves produced on the exit surface of the thin foil. Whereas the average groove length near the beam center is larger than that in the outer areas, the groove width does not change remarkably, suggesting one-directional growth. Oblique irradiation of the (001) foil along [011] changes the groove structure as shown in Fig.1b. Grooves with widths between 1 and 2 nm, which can be seen with strong bright contrast, appear mainly elongated along [100]. A few small grooves elongating along $[01\bar{1}]$ can be seen, of which elongating direction is along [010] if indexed on the (001) foil surface. Circular dark areas can be seen beside the grooves as shown by the arrows. Tilted images revealed that these are hillocks conically growing along the incident beam direction. The very sharp contrast of the grooves observed from the irradiation directions [001] and [011] indicates that the facets of the grooves are imaged almost edge-on, respectively.

For a $(0\bar{1}1)$ oriented foil, grooves generated by [001] irradiation develop rather differently from that for the (001)-oriented foil as shown in **Fig.2a**. Grooves are seen to elongate mainly along the [100] direction with a few short grooves along [010]. One should again note that the elongating direction is along [011] if we index it on the $(0\bar{1}1)$ foil surface. Normal view from $[0\bar{1}1]$ against the foil surface reveals hillocks developing along [001], the beam direction during irradiation (Fig.2b). On the other hand, irradiation normal to the surface along $[0\bar{1}1]$ generates long grooves elongating along [100] with short ones along [011] as shown in **Fig.3a**. Viewed along [001], conically shaped hillocks can be seen to grow along the irradiation direction $[0\bar{1}1]$ as shown by the arrows in Fig.3b. These hillocks correspond to the circular dark areas in Fig.3a.

The groove patterns on the $(0\bar{1}1)$ oriented foil observed from the irradiation directions [001] (Fig.2a) and $[0\bar{1}1]$ (Fig.3a) look similar in spite of the difference in the irradiation direction. However, it is different in the details such as the formation of hillocks, which tend to be conically shaped and often appear far from the grooves in the latter case (see Fig.3). Moreover, the groove pattern produced by $[0\bar{1}1]$ irradiation for the (001) oriented foil is similar to the corresponding irradiation of the $(0\bar{1}1)$ oriented foil. This suggests that the groove patterns which appear for <011> irradiation do

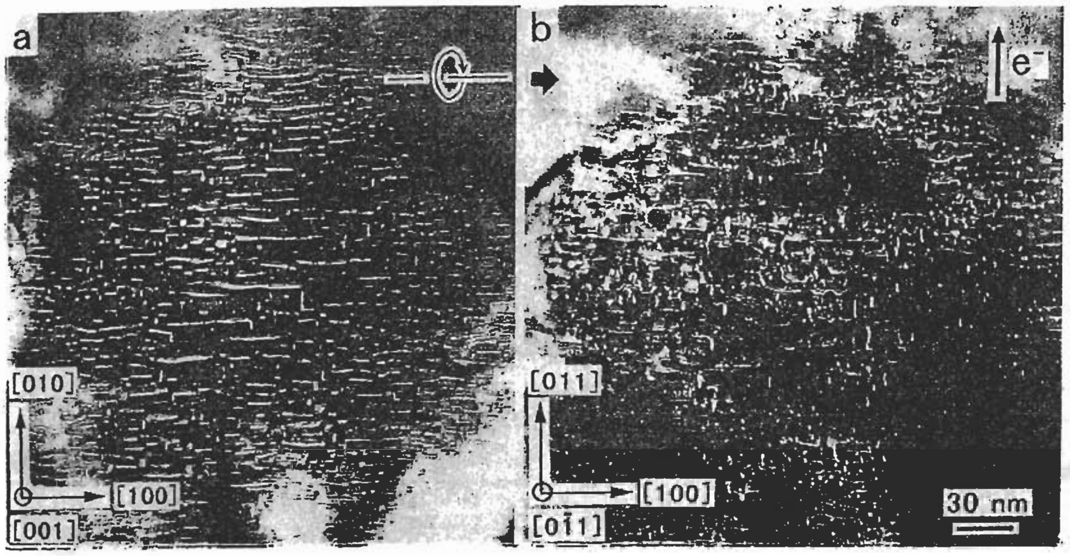

Fig. 2 Electron micrographs of an Au(0$\bar{1}$1) foil irradiated along [001] with 400 keV electrons at 95 K. The foil was rotated around [100] from (a) to (b) as shown in photo (a) and the photos are arranged to observe along (a) [001] and (b) [0$\bar{1}$1] from the eroded surface side. Long grooves and short ones are seen in photo (a) with bright contrast, elongating along [100] and [010], respectively. The short grooves are still seen as bright lines along [011] in (b), indicating that their dominant facets are (100). Hillocks are observed to elongate along the beam direction of [001] in the tilted image of (b).

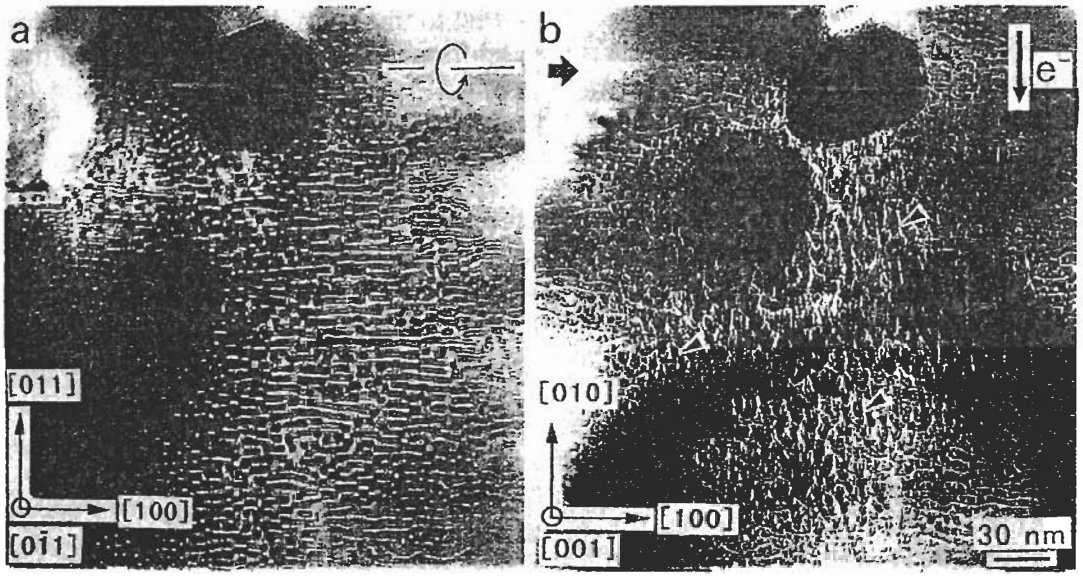

Fig. 3 Electron micrographs of an Au(0$\bar{1}$1) foil irradiated along [0$\bar{1}$1] with 400 keV electrons at 95 K. The foil was rotated around [100] from (a) to (b) as shown in photo (a) and the photos are arranged to observe along (a) [0$\bar{1}$1] and (b) [001] from the eroded surface side. Long grooves and short ones are seen in photo (a) with bright contrast, elongating along [100] and [011], respectively. The short grooves are still seen as bright lines along [010] in photo (b), indicating that their facets are (100). Conically shaped hillocks denoted by arrows in photo (b) are observed to elongate along the beam direction of [0$\bar{1}$1]. These hillocks are observed as dark circular images in photo (a).

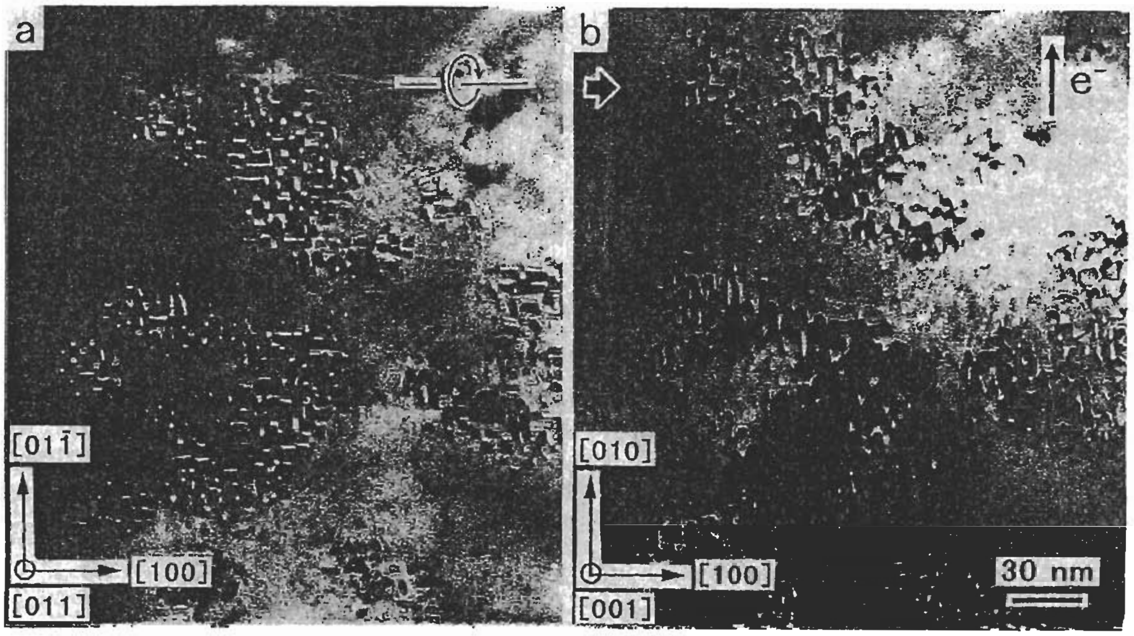

Fig. 4 Uneven appearance of nanogrooves on a thin Au(001) foil irradiated along [011] with 400 keV electrons at 95 K. The foil was rotated around [100] from (a) to (b) as shown in photo (a) and the photos are arranged to observe along (a) [011] and (b) [001] from the eroded surface side. Grooves are seen to be grouped within islands.

not strongly depend on the surface orientation, which is different from the case of <001> irradiation.

Usually nanogrooves are formed uniformly but sometimes appear uneven over the foil surface of the irradiated area as shown in **Fig.4a** for example, which was found for a comparatively thin foil. Grooves are grouped in islands, accompanied by hillocks beside them. The hillocks in Fig.4a shows darker absorption contrast than flat area beside them where grooves are absent, though some are affected by strain contrast. This indicates that the heights of the hillocks is higher compared to the flat area after sputter erosion. The conical shape of the hillocks becomes apparent after tilting by a [100] axis as shown in Fig.4b.

4. Discussion

As clearly shown by the difference in the groove pattern on (001) and (0$\bar{1}$1) surfaces from the same irradiation direction of [001] (Fig.1a and Fig.2a), the groove pattern depends not only on the irradiation direction but also on the foil surface orientation. From the morphological point of view, the groove nature can be characterized by the following two factors, which are respectively shown by solid curves and dotted lines in **Fig.5**:

(a) elongation direction on the foil surface

(b) facets appearing on the side wall of grooves.

Table 1 summarizes the elongating direction and the facet of grooves generated on the (001)- and (0$\bar{1}$1)-oriented foil surfaces by <001> and <011> irradiations. One should note that we have assumed that the side walls of grooves are parallel to the beam direction, judging from the sharp fringe of grooves observed from the beam direction. It is clear that all the long grooves generated both on the (001) and (0$\bar{1}$1) foil surfaces elongate along the [100] direction which is always normal to the irradiation direction, whereas the indices of facets can vary. All the short grooves, on the other hand, can be characterized by the facets. The indices of the facets is always (100) although the elongating direction of grooves can change

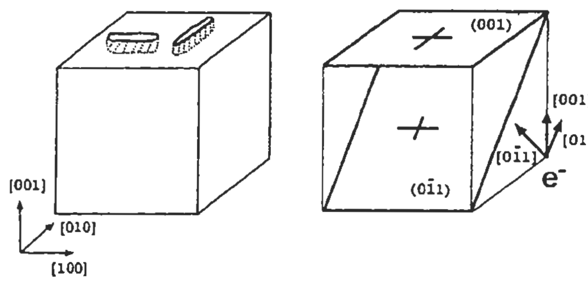

Fig. 5 (a) Schematic views of grooves on (001) surface. Elongating lines of grooves on the surface and the facets are shown by solid curves and dotted line. (b) Elongating lines of grooves generated on (001) and (0$\bar{1}$1) surfaces and electron irradiation directions.

Table 1 Elongating directions and dominant facets of grooves formed on (001)- and $(0\bar{1}1)$-oriented foil surfaces. Relation between the irradiation direction during sputter erosion and the foil surfaces are denoted by N (normal) or O (oblique). Long and short grooves are denoted by L and S. Note that the elongating direction of grooves on the foil surfaces does not always correspond to their projection to the photos from the irradiation direction.

Orientation of foil surface	Irradiation direction	Elongating direction of grooves on foil surface	Facet of side wall of grooves
(001)	[001](N)	[100](L) [010](L)	(010) (100)
	[011](O)	[100](L) [010](S)	$(0\bar{1}1)$ (100)
$(0\bar{1}1)$	[001](O)	[100](L) [011](S)	(010) (100)
	$[0\bar{1}1]$(N)	[100](L) [011](S)	(011) (100)

from [010] for the (001) foil to [011] for the $(0\bar{1}1)$ foil as shown in Table 1.

Similar to this type of groove generation, it has been shown that ion irradiation for amorphous or irradiation induced amorphized materials can produce ripples with wavelengths of the order of 0.1 to 1 μm on their surfaces, developing along directions normal to the beam if the incident beam is close to the surface normal [8]. This ripple generation is theoretically explained by cascade effects near the surface [9]. However, in the present case of groove formation cascade effects play no role due to the low electron kinetic energies used, which enable electrons only to sputter atoms from the surface but not to displace atoms in the bulk of the material [4]. Moreover, oblique electron irradiation along the [112] direction for an Au(001) foil does not produce grooves normal to the beam [7], clearly indicating that the groove formation in the present case is determined by the relation between the surface orientation and the beam direction. As has previously been shown by the appearance of anisotropical self-organized groove patterns close to the critical voltage for sputtering (360kV) [4] where bulk focus collision sequences do not give any anisotropy for sputtering [5], some anisotropical mass transport should exist just on surface for the self-organization process. We assumed the existence of surface collision sequences(SCS) as an origin of one dimensional mass transport.

Uneven appearance of the grooves shown in Fig.4 may give some insight on the anisotropical mass transport on the surface under irradiation. We should note that grooves make colonies, suggesting an enhancement of groove generation beside already formed grooves. This may be explained by a scenario with the SCS diffusion mechanism: At the irradiation temperature where surface vacancies are immobile, their movement will be controlled by irradiation induced diffusion or SCS diffusion mechanism. These can occur by pushing a neighbour atom into the vacancy or by a surface collision sequence (SCS) the last atom of which moves into the vacancy. The latter mechanism leads to a jump of the vacancy corresponding to the length of the collision sequence. If SCSs end at a pre-existing groove they will stop. This means that new grooves preferentially nucleate at a distance from the pre-existing grooves which is comparable to the length of a SCS and along directions which are preferred by the SCS. Moreover, we should note that hillocks exist beside the grooves and their heights are higher than the flat area as mentioned before. These results suggest that a directional mass transport is occurring under irradiation by which surface atoms are carried from the grooves to the hillocks by irradiation induced diffusion or SCS diffusion mechanism.

In order to theoretically predict the shape of groove patterns one has to know into which directions within the surface the electron can transfer most of its energy, leading the preferred directions for the propagation of a SCS. Furthermore one has to consider that the same directions are **not** equivalent on different surfaces. E.g., the atoms surrounding the <100> atom row have different neighbour atoms on {010} and {011} surfaces (the same holds for atom rows along <110>). This might affect the SCS propagation. If the surface is oblique SCSs will hardly occur along directions having a component directed towards the electron beam whereas SCSs with a component parallel to the electron beam will be preferentially excited.

From the above discussion, one can easily guess that the groove pattern may change in various materials if the anisotropy of surface vacancy flow depends on the materials. In fact, a recent experiment on nanogroove formation on the Ag(001) surfaces supports this consideration [7]. Similar to Au, the nanogrooves generated on Ag surfaces showed strong irradiation directional dependencies but the directional features are different from those in Au in spite of the same face-centred cubic structure. The elongating direction of grooves on the Ag(001) surface are along [110] and [1$\bar{1}$ 0] for [001] irradiation, along [100] for [011] irradiation, and along [110] for [112] irradiation. The difference may be attributed to the difference in the anisotropy of SCSs in Au and Ag. It may be interesting to note that differences in the anisotropy of collision sequence propagation in bulk Au and Ag, i.e., along <100> directions for Au but <110> for Ag, which were experimentally supported by a difference in the anisotropy of the threshold energy for atom displacement in both materials [10].

In conclusion, it may be safe to say that the study on the self-organization of anisotropical groove can give some basic insight on the momentum transfer in the surface lattice after incident electron collision. Moreover, it may be technological fruitful if we could utilize this new type of self-organization phenomenon to the nano-structural fabrication.

5. Summary

Au(0$\bar{1}$1) and Au(001) foils were irradiated at 95 K with 400keV electron along the [001] and [0 $\bar{1}$1] directions. It was found that the anisotropical pattern of nanogrooves, generated on the exit surface of thin Au foils by 400keV electron irradiation at 95 K, depends not only on irradiation direction but also on the foil surface orientation. Grooves formed both on the Au(0$\bar{1}$1) and Au(001) foil surfaces are found to be characterized by the elongating direction of [100] and the dominant facets of {100}. In some cases, grooves are found to form colonies and accompany hillocks beside them, suggesting an enhanced generation of grooves beside the preexisting grooves and directional mass transport from grooves towards hillocks. To clarify the self-organized groove formation and the anisotropical mass transport occurring on the surface under irradiation, further experimental and theoretical works are awaited. This type of self-organization phenomenon may be interesting in the view point of the nanostructural fabrication.

References

1. C.J.Humphreys, T.J.Bullough, R.W. Devenish, D.M.Maher and P.S.Turner, Scanning Micros., Suppl. , 4 (1990), 185.
2. P.S. Turner, T.J.Bullogh, R.W.Devenish, D.M.Maher and C.J. Humphereys, Phil.Mag.Lett., 61 (1990), 181.
3. T. Kizuka and N.Tanaka, Phil.Mag.A, (1995), 631.
4. K.Niwase, W.Sigle, F.Phillipp and A.Seeger, Phil.Mag.Lett., 74 (1996), 167.
5. D.Cherns, Surf.Sci., 90 (1979), 339.
6. M.Hohenstein, A.Seeger and W.Sigle, J.Nucl.Mater., 169 (1989), 33.
7. Niwase et al., to be published.
8. For example, G.W.Lewis, M.J.Nobes, G.Carter and J.L.Whitton, Nucl.Instr.and Meth., 170 (1980), 363.
9. R.M.Bradley and J.M.E.Harper, J.Vac.Sci.Technol.A, 6, (1988), 2391.
10. W.Sigle, J.Phys:Condens. Matter 3 (1991), 3921.