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Investigation of $c(2\times 2)$ Phase of Pb and Bi Coadsorption on Cu(001) by Low Energy Electron Diffraction

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The surface phases formed by coadsorption of Pb and Bi on a single crystal Cu(001) surface have been investigated using low energy electron diffraction (LEED). The complete phase chart is developed after the coadsorption of Pb and Bi with various coverages. Some notable phases obtained are (1×1) , $c(2\times 2)$, $c(4\times 4)$ and $c(9\sqrt{2}\times\sqrt{2})$. In this study, we have determined the $c(2\times 2)$ phase. For individual adsorption of both Pb and Bi, we reconfirmed the $c(2\times 2)$ structure with more accuracy by a tensor LEED analysis that they both occupy the four fold hollow sites. By comparing the structural parameters of coadsorption and individual adsorption, we conclude that the $c(2\times 2)$ phase of coadsorption is the mixture of separate domains of the $c(2\times 2)$ phases of Pb and Bi. This study opens a new window of further research into the surface phase determination of coadsorption of Pb and Bi on Cu(001).

Keywords: Coadsorption, Lead, Bismuth, LEED, Phase separation.

1. Introduction

Coadsorption of two dissimilar metals on metal surfaces has been studied for many years. The newly obtained surface materials are a great interest because of their unique structures, chemical compositions, and specific properties. Sometimes these materials are termed as functional nanomaterials¹⁻². To date, for the coadsorption of Pb and Bi, two different metals have been used as substrate. Rh(111) is the recent example of substrate which was studied by Yuhara et al.³. Other one is the Cu. In thin film growth, Cu is largely used because of easiness of its cleaning and it is possible to maintain this cleanliness for a long time. Cu is also used in heterogeneous catalysis as a pure or bimetallic system. Cu-Pb is used as a surfactant to grow the magnetic thin films⁴. On the other hand, Bi is a good magnetic material due to its presence of spin-orbit splitting effect⁵.

The coadsorption of these two heavy metal on Cu(001) substrate was previously studied by Argile and Rhead⁶. Without quantitative measurements, they showed that separate domains of individual Pb and Bi adsorbates occur instead of mixing with each other. Various subsequent experiments have been reported regarding Pb and Bi on Cu, but most of these investigated of diffusion profiles on single crystal Cu⁷⁻⁸ or polycrystalline Cu⁹, and some were bulk alloy studies¹⁰⁻¹². To our best knowledge there is no study of the determination of this system.

In this work, we show the complete phase chart of the

two dimensional surface phases for room temperature coadsorption of Pb and Bi on Cu(001) with the help of low energy electron diffraction (LEED). The obtained phases are (1×1) , $c(2\times 2)$, $c(4\times 4)$ and $c(9\sqrt{2}\times\sqrt{2})$. We then determined the $c(2\times 2)$ phases quantitatively. Before the determination of $c(2\times 2)$ coadsorption, we reconfirm the $c(2\times 2)$ phases of individual adsorption of Pb and Bi on Cu(001) more accurately than in previous reports¹³⁻¹⁵. Our results also show that both types of metal form an overlayer structure. In the case of coadsorption from the $I(E)$ and tensor LEED analysis, it is seen that the $c(2\times 2)$ phase is the mixture of separate $c(2\times 2)$ phases of the individual adsorbates.

2. Experiment and calculation

2.1 Equipment and materials

Experiments were done in an ultrahigh vacuum (UHV) chamber equipped with a four grid LEED system. The base pressure of the UHV chamber was approximately 5×10^{-8} Pa. We used a single crystal Cu(001) of 10 mm diameter and 3 mm thickness as a substrate. To clean the Cu(001) surface, we used several cycles of Ar⁺ sputtering (1 kV, 6.5 μ A, 15 min) and subsequent annealing until a sharp (1×1) LEED pattern was obtained. We then waited for it to become Cu(001) at room temperature. When the sample reached room temperature, Pb and Bi were then deposited by heating them from different sources. After deposition, we used liquid N₂ to

cool the sample. At a temperature of 120 K, the LEED beam spots were measured using a digital charge-coupled device (DCCD) camera with a computer-controlled data acquisition system¹⁶. The temperature was measured by means of a thermometer (Fluke 51 II) attached to the side of the sample. Incident energy range of 100–500 eV was used to obtain the $I(E)$ curves of the LEED beams.

2.2 Theoretical calculation

A Barbieri/Van Hove symmetrized automated tensor LEED package was used to calculate the theoretical $I(E)$ curves for structure models to specify the atomic positions¹⁷. Initially, the calculation of atomic scattering was done by considering 10 phase shifts ($l_{\max}=9$). Although the imaginary part of the inner potential (V_{oi}) was fixed to -5.0 eV but the real part was determined through theory-experiment fit. The best-fit model was obtained based on the best agreement between the experimental and theoretical $I(E)$ curves, which was decided by minimizing Pendry's reliability factor (R_p)¹⁸. The error bar in structural parameters was calculated by variance of R_p , $\Delta R = R_{\min}(8|V_{oi}|/\Delta E)^{1/2}$, where R_{\min} is the minimum R_p value and ΔE is the total energy range of the experimental $I(E)$ curves¹⁸.

3. Results and discussion

3.1 Clean Cu(001) surface

Initially, structure of the clean Cu(001) surface at room temperature was determined by tensor LEED. Figure 1 illustrates the comparison between best-fit and

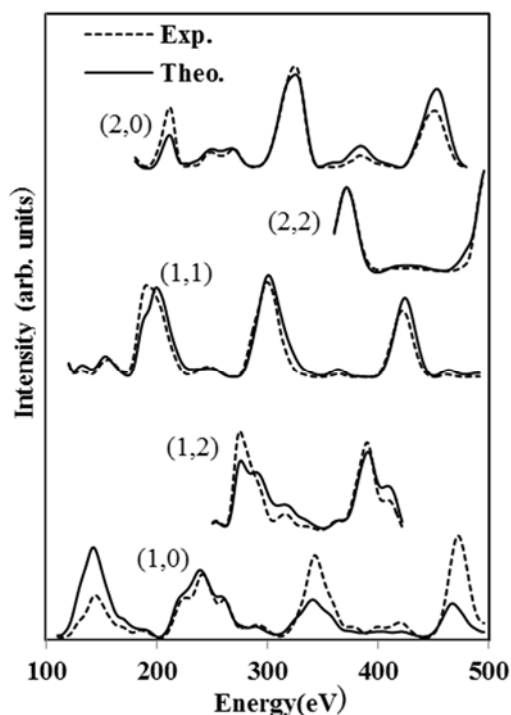


Fig. 1: Best-fit comparison between experimental (dashed lines) and calculated (solid lines) LEED $I(E)$ spectra for clean Cu(001).

experimental spectra for five beams: (1,0), (1,1), (2,0), (2,2) and (1,2). The present LEED $I(E)$ spectra yield the strong evidence of multilayer relaxation in the Cu(001) surface which is similar to the previous studies^{13,19}. This was achieved by obtaining the minimum Pendry $R_p = 0.08$ compared with recent ($R_p = 0.18$)¹³ and earlier report ($R_p = 0.12$)¹⁹. The optimized Debye temperatures for Cu in the first layer and in the next layers were 230 and 343 K, respectively.

The sphere model of surface atoms is shown in Fig. 2. Comparing the bulk interlayer spacing value $d = 1.8075$ Å, it is shown here that a large contraction in the first interlayer spacing of $\Delta d_{12}/d = 2.2 \pm 0.55\%$ causes an expansion in the second interlayer spacing of $\Delta d_{23}/d = 1.2 \pm 0.55\%$. These values can be compared with the latest report¹³: $\Delta d_{12}/d = -1.2 \pm 1.7\%$ and $\Delta d_{23}/d = 1.0 \pm 1.7\%$. The bulk value remains the same for the third and next interlayer spacing as shown in Fig. 2.

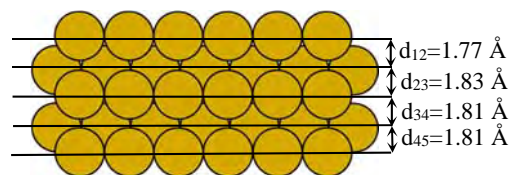


Fig. 2: Surface relaxation in Cu(001).

3.2 c(2×2)-Pb

The c(2×2)-Pb phase is a de-alloying structure that is obtained at a coverage of 0.5, as shown in Fig. 3. The coverage is defined as the ratio of the number of adsorbate atoms to the number of substrate atoms located ideally in a unit cell. Previously¹³⁻¹⁵, it was shown that heavy metals form a substitutional structure at lower coverage (<0.5), whereas it becomes a de-alloying structure at higher coverage (≥ 0.5). Therefore, we carried out the LEED $I(E)$ analysis of this structure for the confirmation with a total energy of 1674 eV. From optimum structural parameters, some features of our study are compared with those of the previous study¹⁴ and are given in Table 1.

We obtained a very good R_p value of 0.19 for this structure. The optimized Debye temperatures for Pb, Cu in the first layer and Cu in the second layer were 80, 260, and 343 K, respectively. The comparison between best-fit $I(E)$ curves and the experimental is given in Fig. 4; the agreement is very good. Here the fourth Cu layer is fixed and all the heights are calculated from this layer. The Cu atoms in the second layer below the Pb atoms move upward (0.02 Å) which was also shown previously for the Bi case¹³. This indicates the attractive interaction between the Cu and Pb atoms.

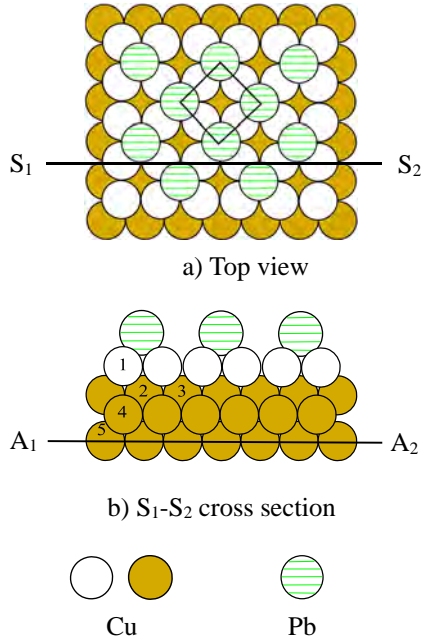


Fig. 3: a) Top and b) cross-sectional views of the best-fit determined structure of Cu(001)- $c(2 \times 2)$ -Pb. The symmetrically inequivalent Cu atoms are numbered. The line A_1 - A_2 marks the fixed Cu layer.

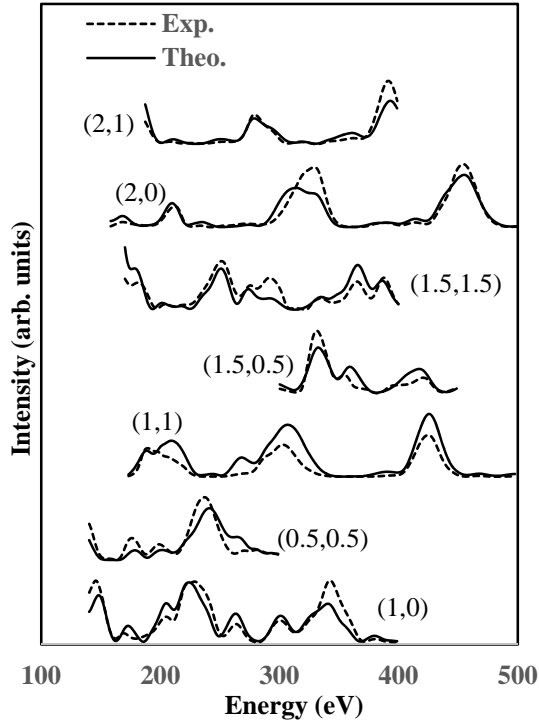


Fig. 4: Best-fit comparison between experimental (dashed lines) and calculated (solid lines) LEED $I(E)$ spectra for Cu(001)- $c(2 \times 2)$ -Pb structure.

Table 1. Comparison of different features of Cu(001)- $c(2 \times 2)$ -Pb obtained in our study and the previous one¹⁴.

Parameters (\AA)	LEED study ¹⁴)	Our Study
Pb-Cu height	2.4 ± 0.05	2.32 ± 0.05
Pb-Cu Bond length	3.0	2.93
Vertical displacement in second Cu layer	Not mentioned	0.02 ± 0.02

3.3 $c(2 \times 2)$ -Bi

As with Pb, the $c(2 \times 2)$ -Bi phase is also a de-alloying structure obtained at a coverage of 0.5. Here, we used total energy of 1746 eV to analyze the LEED $I(E)$ curves. From the optimum structural parameters obtained for this structure, the comparison between our study and previous reports^{13,15} of Bi-Cu height, Bi-Cu bond length, and difference in the second Cu layer is given in Table 2.

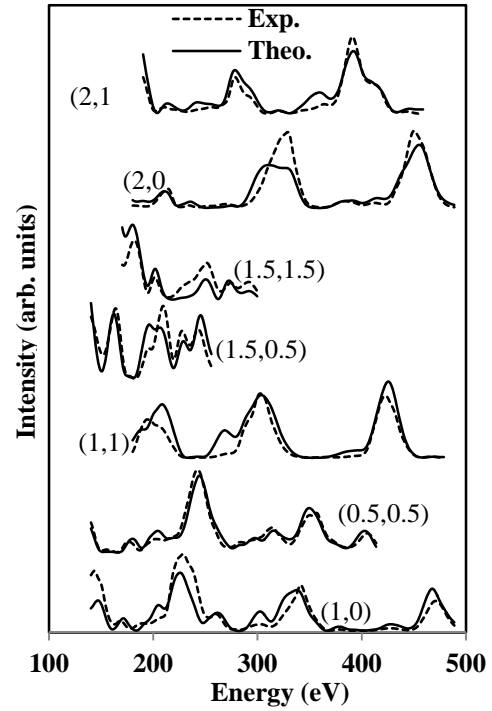


Fig. 5: Best-fit comparison between experimental (dashed lines) and calculated (solid lines) LEED $I(E)$ spectra for Cu(001)- $c(2 \times 2)$ -Bi structure.

Here, we also obtained a very good R_p value of 0.19. The optimized Debye temperatures for Bi, Cu in the first layer, and Cu in the second layer were 90, 260, and 343 K, respectively. The comparison between the best-fit $I(E)$ curves and the experimental ones is given in Fig. 5; the agreement is very good. As with Pb, the Cu atoms in the second layer below the Bi atoms move upward. This

shows the attractive interaction between Bi and Cu atoms.

Table 2. Comparison of different features of Cu(001)–c(2×2)–Bi obtained in our study and the previous one¹³⁾.

Parameters (Å)	LEED study ¹³⁾	Our Study
Bi-Cu height	2.17 ± 0.06	2.22 ± 0.06
Bi-Cu Bond length	2.83	2.86
Vertical displacement in second Cu layer	Not mentioned	0.02 ± 0.02

3.4 Coadsorption of Pb and Bi

The coadsorption of Pb and Bi atoms was performed by depositing these two elements one after the other at various coverages. We started by depositing Pb on Cu(001) at a certain coverage. After that, different coverages of Bi were deposited on the Pb pre-adsorbed surface and LEED patterns were observed. Within a total of one monolayer coverage of Pb and Bi, we obtained (1×1), c(2×2), c(4×4) and c(9√2×√2) LEED patterns as shown in the complete phase chart in Table 3. We obtained the same phase chart when we repeated the coadsorption in reverse order. The important feature here is that although these coadsorption phases could be obtained for individual adsorption of Pb or Bi on Cu(001), we did not obtain the c(5√2×√2) phase that corresponds to the higher coverage (>0.5) of individual Pb on Cu(001). The c(2×2) phase of coadsorption was obtained for different coverage combinations of Pb and Bi, as shown in Table 3. For all combinations, the total coverage of Pb and Bi was in the range 0.5–0.6. The unit cell of the c(2×2) phase at a coverage of ~0.5 correspon-

-ds to one adsorbate atom within two substrate atoms. Hence, with such comparative definition, we can say that the unit cell of the c(2×2) coadsorption phase contains either Pb or Bi atoms. Primarily, we can assume that phase separation into individual adsorbates takes place, and both kinds of adsorbates are not mixed with each other on the surfaces. In the following we will establish our assumption quantitatively.

Firstly, we performed the comparison of experimental $I(E)$ curves obtained from the c(2×2) coadsorption phase with the individual adsorptions of Pb and Bi. From observation, the $I(E)$ spectral shapes were found to be almost similar to each other. Because the individual c(2×2) phase of Pb and Bi at the coverage of 0.5 corresponds to an overlayer structure (as confirmed by previous studies¹³⁻¹⁵⁾ as well as reconfirmed by us, as mentioned above), we predicted that the coadsorption would also make an overlayer structure. Assuming an overlayer structure, we compared the experimental coadsorption data separately with the theoretical $I(E)$ spectra calculated for c(2×2)–Bi and c(2×2)–Pb. For both cases, we obtained a good Pendry R -factor ($R_p = 0.19$) and a good agreement. Fig. 6 shows a comparison between experimental coadsorption data and the theoretical $I(E)$ spectra calculated for both c(2×2)–Pb and c(2×2)–Bi cases. The optimum parameters for both cases of comparison are given in Table 4.

According to our assumption as the c(2×2) phase of coadsorption is the summation of the individual c(2×2) phases of Pb and Bi in separate domains, or a mixture of them in one domain, so the height of Cu-Bi and Cu-Pb must be within the range of their individual c(2×2) phases. Both Cu-Bi and Cu-Pb heights as shown in Table 4 are near the average of their individual cases. This supports our assumption of their separate domains or a mixture of individual c(2×2) phases in a single domain.

Table 3. Phase chart of coadsorption

Pb \ Bi	Coverage	0.1	0.125	0.2	0.25	0.3	0.35	0.4-0.5	0.6-1	
	Phase	1×1					c(4×4)	c(2×2)	c(5√2×√2)	
Coverage										
0.1	1×1	1x1	1×1	c(4×4)	c(4×4)	c(2×2)	c(4×4)	c(4×4)	Δ	
0.125										
0.2										
0.25		c(4×4)	c(4×4)							
0.3				c(2×2)						
0.35						Δ	Δ			
0.4-0.5	c(2×2)	c(2×2)		Δ						
0.6-1	Δ	Δ								

Δ c(9√2×√2)

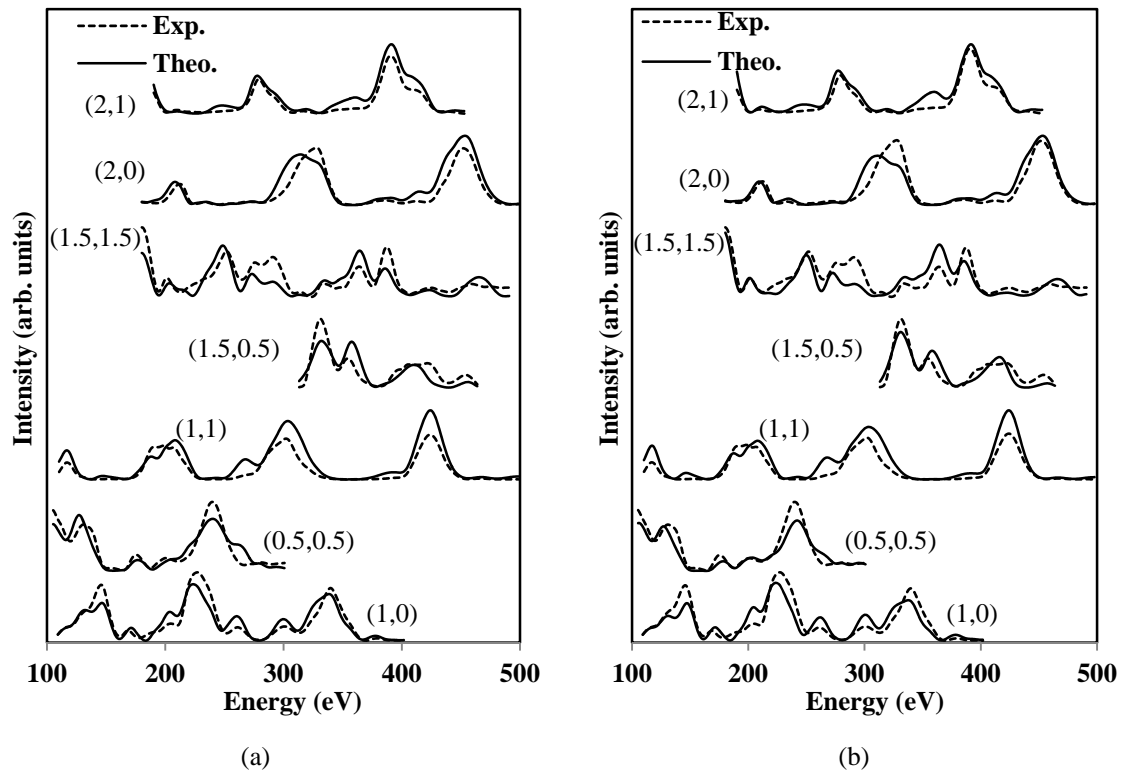


Fig. 6: Best-fit comparison between experimental data of coadsorption (dashed lines) and calculated (solid lines) LEED $I(E)$ spectra for (a) Cu(001)- $c(2 \times 2)$ -Pb, (b) Cu(001)- $c(2 \times 2)$ -Bi

Table 4. Optimum structural parameters for individual Cu(001)- $c(2 \times 2)$ -Pb(Bi) model comparing with experimental $I(E)$ curves for coadsorption

Atom	Height (\AA)	Debye temperature (K)
Pb	2.27 ± 0.05	80
(Bi)	(2.29 ± 0.06)	(90)
Cu ₁	0.00 ± 0.02	260
Cu ₂	1.79 ± 0.02	343
Cu ₃	1.81 ± 0.02	343
Cu ₄	3.61 ± 0.02	343
Cu ₅	5.42	343

The height of Cu₅ was fixed.

Furthermore, because of the similar of atomic masses and characteristics of Pb and Bi, we changed the phase shift of $c(2 \times 2)$ -Pb and $c(2 \times 2)$ -Bi with respect to each other and calculated the theoretical $I(E)$ spectra.

We then compared the experimental coadsorption data with these theoretical $I(E)$ spectra. In both cases, we obtained no effective change of structural parameters but obtained a good fit. This again supports the assertion that either Pb or Bi atoms are located in a unit cell because otherwise we would get a large change in the structural parameters.

A small rippling is shown in the second Cu layer as with the individual adsorption. In this rippling, the Cu atoms underneath of the Pb/Bi atoms move toward the vacuum, which indicates an attractive interaction between the Pb/Bi and Cu atoms.

4. Conclusion

In summary, we conclude that although coadsorption of Pb and Bi on Cu(001) is possible for different combinations of coverage but all of them do not form ternary alloy if the total coverage is greater than or equal to 0.5. For example, in the case of the $c(2 \times 2)$ coadsorption phase, observed near a coverage of 0.6, a phase separation of individual Pb-Cu and Bi-Cu de-alloying occurs and the result of coadsorption is the mixture of these individual phases. For a lower coverage such as 0.375 containing 0.125 of Bi and 0.25 of Pb the $c(4 \times 4)$ phase is obtained. This is reported as an ordered ternary alloy of Pb-Cu-Bi, which will be discussed elsewhere.

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References

- 1) C. B. Duke and E. W. Plummer, *Frontiers in Surface and Interface Science*, 1st edition, Elsevier, Netherlands (2002)
- 2) H. W. Yeom, S. Takeda, E. Rotenburg, I. Matsuda, K. Horikoshi, J. Schaefer, C. M. Lee, S. D. Kevan, T. Ohta, T. Nagao, and S. Hasegawa, *Physical Review Letters*, **82**, 4898 (1999).
- 3) J. Yuhara, M. Yokoyama and T. Matsui, *Journal of Applied Physics*, **110**, 074314 (2011).
- 4) D.P. Woodruff, *Surface Alloys and Alloy Surfaces*, 1st edition, Elsevier, Netherlands (2002).
- 5) Ph. Hofmann, *Progress in Surface Science*, **81**, 191 (2006).
- 6) C. Argil and G.E. Rhead, *Surface Science*, **78**, 115 (1978).
- 7) P. Monchoux, D. Chatain and P. Wynblatt, *Surface Science*, **601**, 1101 (2007).
- 8) J. Moon, P. Wynblatt, S. Garoff and R. Suter, *Surface Science*, **559**, 149 (2004).
- 9) J. Monchoux, D. Chatain and P. Wynblatt, *Surface Science*, **575**, 69 (2005).
- 10) D. Manasijevic, A. Mitovskia, D. Minic, D. Zivkovic, S. Marjanovic, R. Todorovic and L. Balanovic, *Thermochimica Acta*, **503-504**, 115 (2010).
- 11) D. Zivcovic, D. Mansijevic and Z. Zivkovic, *Thermochimica Acta* **417**, 119 (2004).
- 12) X.W. Hu, S.M. Li, S.F. Gao, L. Liu and H.Z. Fu, *Journal of Alloys and Compounds*, **501**, 110 (2010).
- 13) E. Alshmaileh and C. Barnes, *Physical Chemistry Chemical Physics*, **4**, 5148 (2002).
- 14) W. Hoesler and W. Moritz, *Surface Science*, **117**, 196 (1982).
- 15) H. L. Meyerheim, H. Zajonz, W. Moritz and I. K. Robinson, *Surface Science*, **381**, L551 (1997).
- 16) S. Mizuno, H. Tochiyama, A. Barbieri and M.A. Van Hove, *Physical Review B*, **52**, R11658 (1995).
- 17) M.A. Van Hove, W. Moritz, H. Over, P.J. Rous, A. Wander, A. Barbieri, N. Materer, U. Starke and G. A. Somorjai, *Surface Science Reports*, **19**, 191 (1993).
- 18) J.B. Pendry, *Journal of Physics C: Solid State Physics*, **13**, 937(1980).
- 19) D. M. Lind, F. B. Dunning, G. K. Walters and H. L. Davis, *Physical Review B*, **35**, 9037 (1987).