Surface structure of bulk 2H-MoS₂(0001) and exfoliated suspended monolayer MoS₂: A selected area low energy electron diffraction study

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Abstract

We have used selected area low energy electron diffraction intensity-voltage (μ LEED-IV) analysis to investigate the surface structure of crystalline 2H molybdenum disulfide (MoS₂) and mechanically exfoliated and suspended monolayer MoS₂. Our results show that the surface structure of bulk 2H-MoS₂ is distinct from its bulk and that it has a slightly smaller surface relaxation at 320 K than previously reported at 95 K (Van Hove et al., 1977). We concluded that suspended monolayer MoS₂ shows a large interlayer relaxation compared to the MoS₂ sandwich layer terminating the bulk surface. The Debye temperature of MoS₂ was concluded to be about 600 K, which agrees with a previous theoretical study (Su et al., 2015). Our work has shown that the dynamical μ LEED-IV analysis performed with a low energy electron microscope (LEEM) is a powerful technique for determination of the local atomic structures of currently extensively studied two-dimensional (2-D) materials.

Keywords: MoS₂, μ LEED-IV, 2-D material, surface structure

1. Introduction

Molybdenum disulfide (MoS₂), a layered transition metal dichalcogenide, is an indirect-gap semiconductor with an optical band gap matching well with the solar spectrum [1]. Due to this important property, it may be used for electrodes in high efficiency photoelectrochemical (PEC) cells [2]. MoS₂ has three common polytypes: 1T-MoS₂, 2H-MoS₂ and 3R-MoS₂. The 2H-MoS₂ polytype is the most stable configuration [3]. The present study investigates 2H-MoS₂; its crystal structure is shown in Fig. 1. MoS₂ consists of covalently

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Figure 1: Crystal structure of 2H-MoS₂, dashed quadrangular prism indicates the unit cell. $a = 3.16 \text{ \AA}$, $z = 1.593 \text{ \AA}$, $w = 2.959 \text{ \AA}$ [9].

bonded S-Mo-S sandwich layers. The unit cell of bulk 2H-MoS₂ consists of two symmetrically inequivalent S-Mo-S sandwich layers. Each sandwich layer is characterized by strong intralayer covalent bonding, whereas the sandwich layers bond to each other via weak interlayer van der Waals' forces. While the electronic structure [4, 5, 6] and crystal structure [7, 8] of bulk MoS₂ have been studied extensively, there have been very few studies on the surface structure. The only low energy electron diffraction (LEED-IV) study was conducted by Van Hove *et al.*, which reported that the surface remained mostly unchanged from its bulk structure except that the first interlayer spacing is contracted by 4.7% and the first sandwich interlayer spacing is contracted by 3% at the temperature of 95 K [9, 10]. This study assumed the second interlayer spacing remained unchanged from that of bulk MoS₂ [9]. A coaxial impact-collision ion scattering spectroscopy (CAICISS) study reported that the first interlayer spacing has a contraction of 3.6% while the second interlayer spacing has an estimated contraction of 0 to 2% at room temperature [11]. However the CAICISS study was only able to determine the first two interlayer spacings and the second interlayer spacing was not accurately determined. The goals of our paper is to determine the surface structure of this important photovoltaic material at an elevated temperature of 320 K using μ LEED-IV analysis.

Monolayer MoS₂ can be prepared through mechanical exfoliation from bulk MoS₂ [12] and it has very different electronic properties compared to crystalline MoS₂ [13]. Most striking is the transition from an indirect to direct band gap semiconductor behavior when going from bulk to monolayer [14]. Due to its unique properties, monolayer MoS₂ has been suggested to be an ideal candidate for applications in atomically thin, layered electronics [15, 16], optical [17, 18], and photovoltaic [19] devices. Thus it is essential to know the atomic structure of monolayer MoS₂ in order to better understand its properties and provide guidance to its applications. For monolayer MoS₂, the absence of interlayer interaction and the presence of substrate interaction may lead to crystalline structure distortion and surface morphology roughness, and as a result, these may modify its key properties. Therefore, the preservation

of its intrinsic properties is crucial to the potential applications of monolayer MoS₂. Various aspects of monolayer MoS₂, including electronics, optics, spintronics, and valleytronics, have been extensively investigated; however, the number of studies of the atomic structure, especially surface structure is quite limited. Here, we study the atomic structure of monolayer MoS₂ in two systems: the surface of bulk 2H-MoS₂, which is a good approximation of an isolated monolayer, due to the natural break in the perpendicular periodicity and the weak van der Waals interaction with the bulk underneath, and the suspended monolayer MoS₂. To date, there has been no detailed study of the atomic structure of the monolayer MoS₂. To resolve the surface structure of monolayer MoS₂, the characterization technique needs to have: (1) high lateral resolution, since currently prepared monolayer MoS₂ flakes are usually only a few μm in size and (2) sensitivity to the atomic positions in few-layer samples. So far, dynamical $\mu\text{LEED-IV}$ analysis remains the only plausible technique that possesses both functionalities [20, 21, 22]. In the present work, we have used μLEED with a small sampling areas of 5 μm diameter, combined with dynamical LEED-IV analysis, to investigate the atomic structure of monolayer MoS₂.

2. Experiment

Large multiple layer MoS₂ flakes (lateral dimension $> 10\mu\text{m}$) were mechanically exfoliated and transferred onto a Si wafer with poly(methyl methacrylate) (PMMA) and polyvinyl alcohol (PVA) overlayers using the methods detailed in [14, 23]. The MoS₂ flakes were characterized using optical microscopy and their thickness was also determined using Raman [24] and photoluminescence spectroscopy [25]. Thick MoS₂ flakes (> 100 layers) of about 10 μm diameter were prepared, as shown in Fig. 2(a), and considered equivalent to bulk MoS₂. Prior to measurements, the samples were annealed at 350°C for 6 hours in ultrahigh vacuum to remove contaminants. Our experiment was carried out on the Spectroscopic Low Energy Electron Microscope (SPE-LEEM) system at the National Synchrotron Light Source beamline U5UA. LEEM was used to locate the sample area of interest, as shown in Fig. 2(a). Subsequently, the crystalline structure of the sample was investigated using μLEED with a 5 μm sampling area. μLEED of monolayer (1 ML), bilayer (2 ML), trilayer (3 ML) and bulk MoS₂ (more than 100 layers thick) flakes shows well-defined hexagonal patterns with 3-fold symmetry (see Fig. 2). The linewidth of the μLEED spots increases with decreasing sample thickness (see Fig. 3(a)). This phenomenon is attributed to the surface corrugation induced by the interaction with the substrate [12, 23]. The surface corrugation can be further quantitatively characterized using the model $\Delta\theta = \Delta k_{\parallel} / 2k_0$ [26, 27], where $\Delta\theta$ is the standard deviation of the local surface normal, $\Delta k_{\parallel}$ is the linewidth of the central diffraction spots (denoted as (00) beam), and $k_0 = \sqrt{2m_e E_{kin}}$ is the incident electron momentum.

We performed *in situ* intensity *vs* voltage measurements in reciprocal space (LEED-IV). Data were collected using a normal incident electron beam with energy ranging from 25-150 eV. As shown in Fig. 3(b), the linewidth of the diffraction spots increase linearly with k_0 . In addition, the magnitude of surface roughness of 1 ML MoS₂ is strikingly large in comparison with 2-3 ML and bulk MoS₂, indicating a strong substrate interaction. Figure 2(c), 2(d) and 2(e) show the LEED patterns of bulk MoS₂ acquired at 40 eV, 78 eV, and 95 eV,

Figure 2: (a) LEEM image of bulk, 1 ML, 2 ML and 3 ML MoS₂ on Si substrate; (b) 1 ML suspended MoS₂; μ LEED patterns of bulk MoS₂ acquired at (c) 40 eV, (d) 78 eV, and (e) 95 eV, respectively. Note that (c) and (e) clearly display 3-fold symmetry.

respectively.

Furthermore, we combined μ LEED-*IV* measurements with dynamical LEED calculations to determine the atomic surface structure. In our LEED-*IV* curves, the intensity of (01) and (10) beam is the average intensity of the three symmetrically equivalent diffraction spots denoted as A and B in Fig. 2(c), respectively. The averaging procedure above seeks to minimize the intensity anisotropy of the diffraction beam due to small sample tilting ($< 0.1^\circ$). The background intensity was subtracted from the scattered beam intensity.

To obtain suspended MoS₂, we fabricated the substrate by patterning cylindrical cavities (2 or 5 μ m in diameter and 1 μ m in depth) on an n-doped Si wafer with native oxide using lithography and etching. Subsequently, the monolayer MoS₂ flake was transferred onto the patterned substrate using the same transfer method as used for bulk MoS₂ flakes. As a result, we obtain suspended monolayer MoS₂ over the cavity regions. The different electron reflectivity of suspended and supported monolayer MoS₂ and the substrate exhibit clear contrast, as shown in Fig. 2(b). This allows us to carry out μ LEED measurements at the regions of interest; LEED-*IV* of six first order diffracted beams (three (10) beams and three

Figure 3: (a) Intensity profiles of the (00) diffraction beam of 1-3 ML and bulk MoS₂. (b) Linewidth of the (00) diffraction beam as a function of k_0 , $k_0 = \sqrt{2m_e E_{kin}}$

(01) beams) for the energy range of 25-100 eV were extracted from the experiment. The (00) beam was too diffuse to extract *IV* data; this is likely due to reflection from the edges of the cavity.

3. Calculation details

We performed a dynamical LEED-*IV* analysis of our μ LEED data collected by LEEM from the bulk MoS₂ flake and the suspended monolayer MoS₂. In a dynamical LEED-*IV* analysis, *IV* curves are calculated for a trial structure and compared with experimental curves. The optimized structural parameters are, the first three interlayer spacings for bulk MoS₂ and the first two interlayer spacings for the monolayer MoS₂. These spacings are adjusted to give the best agreement with the measured *IV* curves. A χ^2 -based R_2 factor is employed to quantify the agreement level between the experimental and theoretical data [28]. The error bars in the surface structure analysis are based on an increase of 4% in the R_2 factor [21]. To calculate the *IV* curves, we used computer codes from Adams *et al.* [28] which were developed from the programs of Pendry [29] and Van Hove and Tong [30]. The advantage of Adams' code set is the fact that the relative intensities of diffraction beams are preserved during the optimization. The phase shifts (a quantity describing the atomic scattering property [30]) were calculated using the Barbieri/Van Hove phase shift calculation package [31]. The muffin-tin radii for Mo atom and S atom are set to $r_{Mo}^{MT} = 2.4598$ a.u. and $r_S^{MT} = 2.1084$ a.u., respectively. 12 phase shifts ($L = 11$) were used for the

LEED-*IV* calculation. The in-plane lattice constant was $a = 3.16$ Å, the Mo and S atomic layer distance was $z = 1.593$ Å and the layer distance between the S-Mo-S sandwich layers was $w = 2.959$ Å for the bulk, as indicated in Fig. 1(b) [9]. The interlayer spacing between the i th and j th surface atomic layer is indicated as d_{ij} .

The mean-square atomic vibrational displacements $\langle u^2 \rangle_T$ for Mo and S were calculated individually according to the relation between Debye temperature θ_D and $\langle u^2 \rangle_T$ at the sample temperature T (320 K) using the following equation [29]:

$$\langle u^2 \rangle_T = \frac{9\hbar^2}{m_a k_B \theta_D} \left\{ \frac{T^2}{\theta_D^2} \int_0^{\frac{\theta_D}{T}} \frac{x dx}{e^x - 1} + \frac{1}{4} \right\} \quad (1)$$

where m_a is the atomic mass, $\hbar$ is the Planck's constant and k_B is the Boltzmann constant. Two Debye temperatures θ_D were tested for MoS₂: 350 K [9] and 600 K [32]. The inner potential, $V_0 + iV_{im}$, was set to be independent of energy. The real part V_0 was initially set to be 8 eV and adjusted through ΔV_0 (the decrease in V_0) during the fitting process and the imaginary part V_{im} was set to be 6 eV.

4. Results and discussion

Among the two Debye temperatures θ_D we examined (350 K and 600 K), $\theta_D = 600$ K shows a slightly better agreement between the calculated *IV* curves and the experiment, which agrees with a previous study [32] that found that the Debye temperature increases and approaches a constant as temperature increases for layered materials. Specifically, the Debye temperature of MoS₂ approaches 600 K when the temperature rises above room temperature. Another neutron scattering study reported that the high-temperature Debye temperature is almost twice as large as that of zero temperature [33]. This behavior seems to be common to materials that have large c-lattice constants and extremely weak interlayer interactions.

To refine the surface atomic structure, the structure was relaxed and a search for small variations compared to the bulk was carried out. Fig. 4 shows heat maps of the R_2 factor as a function of the surface structural parameters d_{12} and d_{13} for bulk MoS₂ surface (left) and suspended monolayer MoS₂ (right). It clearly shows a well-defined R_2 factor minimum for both cases. Best-fit structural parameter values are listed in Table 1 and compared with previously reported results [9, 10, 11]. Comparisons of experimental to calculated *IV* curves are shown in Fig. 5. Small R_2 factors [28] of 0.086 and 0.102 were achieved for bulk MoS₂ and monolayer, respectively. This indicates good agreement between the calculated and experimental *IV* curves as shown in Fig. 5. The optimized bulk MoS₂ structural results show that the topmost interplanar spacing d_{12} has a smaller contraction of $2.5 \pm 1.9\%$ from its bulk value at 320 K, compared with a contraction of 4.7% at 95 K [9, 10]. The second interplanar spacing d_{23} contracted by $1.3 \pm 2.5\%$. The first vdW (van der Waals) gap shows an expansion of $1.3 \pm 2.7\%$ at 320 K from its bulk value instead of a contraction of 3% at 95 K [9, 10]. Since we fabricated MoS₂ flakes with high-quality surfaces, the differences of the surface structures between this work and previous studies [9, 10] is less likely due to the

Figure 4: Heat maps of the R_2 factor as a function of surface structural parameters d_{12} and d_{13} for bulk MoS₂ (left) and suspended monolayer MoS₂ (right).

different preparation methods. We attempt to attribute the difference to thermal expansion of 2H-MoS₂ [34, 35] at elevated temperature in our measurement.

Based on our dynamical calculations and optimized results, the suspended monolayer MoS₂ has a slightly different structure compared to the S-Mo-S sandwich layer terminating the bulk surface. The first interlayer spacing d_{12} is slightly expanded by $1.3 \pm 1.9\%$ compared to the bulk value while the second interlayer spacing d_{23} is contracted by $5.1 \pm 3.8\%$ compared to the bulk value, as presented in Table 1. For an isolated monolayer of MoS₂, one would expect that the two layer spacings, d_{12} and d_{23} to be identical, since the molybdenum layer is centered between the two sulfur layers, as in the bulk crystalline structure. The slight asymmetry of the interlayer spacings might be caused by a small amount of warping or strain [12] of the suspended monolayer. Due to the limited sample size, shorter energy range of 25-100 eV and only six accessible beams for monolayer MoS₂, our conclusion for the atomic structure of the monolayer MoS₂ is potentially less reliable. The observed slight increase in the thickness of the topmost S-Mo-S sandwich layer of bulk MoS₂, $d_{13} = 3.13 \pm 0.04$ Å, as well as suspended monolayer MoS₂, $d_{13} = 3.13 \pm 0.06$ Å, at 320 K compared to previous result for the bulk surface at 95 K, $d_{13} = 3.11$ Å, is not significant within our error bars.

There is a systematic disagreement between the calculated IV curves and the measured ones at the energy range between 50-60 eV while the calculations produced the main features of the measured IV curves over the rest of the energy range. We attribute this discrepancy to the strong back scattering of the electrons from the substrate and the sample flake boundary at this energy range. This was confirmed by observation of an unexpected peak at the range of 50-60 eV in the background IV curve.

(a) (00) beam, bulk 2H-MoS₂

(b) (10) beam, bulk 2H-MoS₂

(c) (01) beam, bulk 2H-MoS₂

(d) (10) beam, monolayer MoS₂

(e) (01) beam, monolayer MoS₂

Figure 5: Comparison of experimental and calculated I - V curves for bulk 2H-MoS₂ and suspended monolayer MoS₂ for measured diffraction spots.

Table 1: Optimum parameter values for the surface structure of 2H-MoS₂(0001)

Model	T	d_{12} (Å) ($\Delta d_{12}/z$)	d_{23} (Å) ($\Delta d_{23}/z$)	d_{13} (Å) ($\Delta d_{13}/2z$)	d_{34} (Å) ($\Delta d_{34}/w$)
Ref. [9, 10] (Bulk MoS ₂)	95 K	1.518 (-4.7%)	1.593 (fixed bulk value)	3.111 (-2.4%)	2.877 (-2.8%)
Ref. [11] (Bulk MoS ₂)	300 K	1.536 (-3.6%)	1.561 ~ 1.593 (-2% ~ 0%)	3.097 ~ 3.129 (-2.8% ~ -1.8%)	N. A.
This work (Bulk MoS ₂)	320 K	1.553±0.03 (-2.5±1.9%)	1.573±0.04 (-1.3±2.5%)	3.126±0.04 (-1.9±1.3%)	2.99±0.08 (+1.3±2.7%)
This work (Monolayer)	320 K	1.613±0.03 (+1.3±1.9%)	1.513±0.06 (-5.1±3.8%)	3.126±0.06 (-1.9±1.9%)	N. A.

5. Conclusion

In conclusion, we showed that dynamical μ LEED- IV analysis is a potentially powerful candidate for determination of the atomic structure of 2-D materials. We concluded that at a sample temperature of 320 K, the Debye temperature of MoS₂ was about 600 K, which agrees with a previous study [32]. Good agreement was achieved between the measured IV curves and calculated IV curves for both the surface of the bulk MoS₂ and monolayer MoS₂. Our work also showed that the surface structure of bulk 2H-MoS₂ is distinct from its bulk crystalline structure and the surface structure is different at 320 K from its structure at 95 K due to thermal surface expansion. The interlayer spacing between the very top S atomic layer and the first Mo layer, d_{12} , has a smaller contraction of 2.5% at 320 K than at 95 K. The layer spacing between the first Mo atomic layer and the second S layer, d_{23} , has a small contraction of 1.3% from the bulk. We also showed that the layer spacing between the first S-Mo-S sandwich layer and the second sandwich layer, d_{34} , has an small expansion of 1.3% at 320 K compared to a contraction at 95 K. Finally we have concluded with less certainty, that the suspended monolayer MoS₂ has a large interlayer relaxation compared to the S-Mo-S sandwich layer terminating the bulk surface: d_{12} is expanded by 1.3% and d_{34} is contracted by 5.1% compared to the respective bulk value.

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References

- [1] T. Böker, R. Severin, A. Müller, C. Janowitz, R. Manzke, D. Voß, P. Krüger, A. Mazur, J. Pollmann, *Phys. Rev. B* 64 (2001) 235305.
- [2] X. Xu, J. Hu, Z. Yin, C. Xu, *ACS Appl. Mater. Interfaces* 6(8) (2014) 5983–5987.
- [3] Y. Fu, X. Feng, M. Yan, K. Wang, S. Wang, *Physica B: Condensed Matter* 426 (2013) 103–107.
- [4] R. Coehoorn, C. Haas, J. Dijkstra, C. Flipse, R. de Groot, A. Wold, *Phys. Rev. B* 35 (1987) 6195.
- [5] S. W. Han, G.-B. Cha, E. Frantzeskakis, I. Razado-Colambo, J. Avila, Y. S. Park, D. Kim, J. Hwang, J. S. Kang, S. Ryu, W. S. Yun, S. C. Hong, M. C. Asensio, *Phys. Rev. B* 86 (2012) 115105.
- [6] S. K. Mahatha, K. S. Menon, *J. Phys. Condens. Matter* 24 (2012) 305502.
- [7] R. G. Dickinson, L. Pauling, *J. Am. Chem. Soc.* 45(6) (1923) 1466–1471.
- [8] J. Wilson, A. Yoffe, *Adv. Phys.* 18 (73) (1969) 193–335.
- [9] B. J. Mrstik, R. Kaplan, T. L. Reinecke, M. V. Hove, S. Y. Tong, *Phys. Rev. B* 15 (1977) 897.
- [10] M. V. Hove, S. Tong, M. Elconin, *Surf. Sci.* 64 (1977) 85–95.
- [11] Y. Kadowaki, K. Aika, H. Kondoh, H. Nozoye, *Physica B: Condensed Matter* 426 (2013) 103–107.
- [12] W. Jin, P.-C. Yeh, N. Zaki, D. Zhang, J. T. Liou, J. T. Sadowski, A. Barinov, M. Yablonskikh, J. I. Dadap, P. Sutter, I. P. Herman, R. M. Osgood, *Phys. Rev. B* 91 (2015) 121409.
- [13] S. Z. Butler, S. M. Hollen, L. Cao, Y. Cui, J. A. Gupta, H. R. Gutiérrez, T. F. Heinz, S. S. Hong, J. Huang, A. F. Ismach, E. Johnston-Halperin, M. Kuno, V. V. Plashnitsa, R. D. Robinson, R. S. Ruoff, S. Salahuddin, J. Shan, L. Shi, M. G. Spencer, M. Terrones, W. Windl, J. E. Goldberger, *ACS Nano* 7 (4) (2013) 2898–2926.
- [14] W. Jin, P.-C. Yeh, N. Zaki, D. Zhang, J. T. Sadowski, A. Al-Mahboob, A. M. van der Zande, D. A. Chenet, J. I. Dadap, I. P. Herman, P. Sutter, J. Hone, R. M. Osgood, *Phys. Rev. Lett.* 111 (2013) 106801.
- [15] B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, A. Kis, *Nat. Nanotechnol.* 6 (2011) 147–150.
- [16] L. Britnell, R. V. Gorbachev, R. Jalil, B. D. Belle, F. Schedin, A. Mishchenko, T. Georgiou, M. I. Katsnelson, L. Eaves, S. V. Morozov, N. M. R. Peres, J. Leist, A. K. Geim, K. S. Novoselov, L. A. Ponomarenko, *Science* 344 (2012) 947–950.
- [17] K. F. Mak, C. Lee, J. Hone, J. Shan, T. F. Heinz, *Phys. Rev. Lett.* 105 (2010) 136805.
- [18] Z. Yin, H. Li, H. Li, L. Jiang, Y. Shi, Y. Sun, G. Lu, Q. Zhang, X. Chen, H. Zhang, *ACS Nano* 6(1) (2012) 74–80.
- [19] M. Fontana, T. Deppe, A. K. Boyd, M. Rinzan, A. Y. Liu, M. Paranjape, P. Barbara, *Sci. Report.* 3 (2013) 1634.
- [20] J. Sun, J. B. Hannon, R. M. Tromp, P. Johari, A. A. Bol, V. B. Shenoy, K. Pohl, *ACS Nano* 4(12) (2010) 7073.
- [21] J. Sun, J. B. Hannon, G. L. Kellogg, K. Pohl, *Phys. Rev. B* 76 (2007) 205414.
- [22] J. de la Figuera, J. Puerta, J. Cerda, F. E. Gabaly, K. McCarty, *Surf. Sci.* 600 (2006) L105.
- [23] P.-C. Yeh, W. Jin, N. Zaki, D. Zhang, J. T. Sadowski, A. Al-Mahboob, A. M. van der Zande, D. A. Chenet, J. I. Dadap, I. P. Herman, P. Sutter, J. Hone, R. M. Osgood, *Phys. Rev. B* 89 (2014) 155408.
- [24] C. Lee, H. Yan, L. E. Brus, T. F. Heinz, J. Hone, S. Ryu, *ACS Nano* 4 (2010) 2695.
- [25] A. Splendiani, L. Sun, Y. Zhang, T. Li, J. Kim, C.-Y. Chim, G. Galli, F. Wang, *Nano Lett.* 10 (2010) 1271.
- [26] M. Ishigami, J. H. Chen, W. G. Cullen, M. S. Fuhrer, E. D. Williams, *Nano Lett.* 7 (2007) 1643.
- [27] K. R. Knox, S. Wang, A. Morgante, D. Cvetko, A. Locatelli, T. O. Montes, M. A. Nio, P. Kim, J. R. M. Osgood, *Phys. Rev. B* 78 (2008) 201408.
- [28] D. L. Adams, *Surf. Sci.* 519 (2002) 157–172.
- [29] J. B. Pendry, *Low-Energy Electron Diffraction*, Academic (London) 1974.
- [30] M. V. Hove, S. Y. Tong, *Surface Crystallography by LEED*, Springer-Verlag (Berlin) 1979.
- [31] A. Barbieri, M. V. Hove, packages available online: <https://www.icts.hkbu.edu.hk/vanhove/> (accessed 14.07.2016).
- [32] J. Su, Z.-T. Liu, L.-P. Feng, N. Li, *J. Alloys Compd.* 622 (2015) 777–782.
- [33] N. Wakabayashi, H. G. Smith, R. M. Nicklow, *Phys. Rev. B* 12 (1975) 659.

- [34] S. H. El-Mahalawy, B. L. Evans, J. Appl. Cryst. 9 (1976) 403.
- [35] R. Murray, B. L. Evans, J. Appl. Cryst. 12 (1979) 312.