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Research Article

Absence of the Rashba Splitting of Au(111) Surface Bands

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The electronic structure of Au(111) films is studied by means of relativistic DFT calculations. It is found that the twinning of the surface bands, observed in photoemission experiment, does not necessarily correspond to the spin-splitting of the surface states caused by the break of the inversion symmetry at the surface. The twinning of the bands of clean Au(111) films can be obtained within nonrelativistic or scalar-relativistic approximation, so that it is not a result of spin-orbit coupling. However, the spin-orbit coupling does not lead to the spin-splitting of the surface bands. This result is explained by Kramers' degeneracy, which means that the existence of a surface itself does not destroy the inversion symmetry of the system. The inversion symmetry of the Au(111) film can be broken, for example, by means of adsorption, and a hydrogen monolayer deposited on one face of the film indeed leads to the appearance of the spin-splitting of the bands.

1. Introduction

The twin surface bands of Au(111) with a parabolic dispersion, pertinent to nearly free electrons, were found in angle-resolved photoemission study by LaShell et al. [1] and explained as a result of the spin-splitting caused by spin-orbit coupling (SOC). Probably, this interpretation, in large part, was inspired by a rapidly growing interest to so-called topological insulators [2–5] and, in this regard, to the Rashba splitting [6–8] of surface bands crossing E_F. One of the most persuasive arguments in support of this explanation was the absence of the splitting at Γ (the center of the Brillouin zone), which seemingly indicated that the splitting of the surface bands for $\mathbf{k}_{||} \neq 0$ was allowed due to an absence of inversion symmetry at the surface and thus the lifting of Kramers' degeneracy. (Recall that the inversion symmetry of a crystal $E(-\mathbf{k}, \uparrow) = E(\mathbf{k}, \uparrow)$ together with the time-reversal symmetry $E(-\mathbf{k}, \uparrow) = E(\mathbf{k}, \downarrow)$ leads to $E(\mathbf{k}, \uparrow) = E(\mathbf{k}, \downarrow)$, that is, to the spin degeneracy of the bands for all $\mathbf{k}$.)

However, as noted by Reinert [9], since these results were not reproduced over several years and the splitting of the bands was not observed by means of the scanning tunneling spectroscopy [10], this interpretation was later questioned, and different mechanisms, such as the herringbone reconstruction of the Au(111) surface [11], were proposed to explain the splitting of the surface bands. On the other hand, the Rashba-type splitting of the surface bands was later supported by tight-binding calculations [12] and photoemission studies (also for similar surface states of Ag(111) and Cu(111) [13]) and first-principles calculations for Au(111) slabs [14].

The theory of the Rashba effect [6] is based on the model of a 2D electron gas, which might be applicable for true surface states in semiconductor heterostructures, but obviously not for surface resonances in metals. Indeed, the degree of the localization of the surface resonances of Au(111) is relatively weak and this feature causes a significant interaction between the surface states of opposite surfaces even for rather thick (up to ~20 monolayers) Au(111) films [14]. For this reason, as was noted by Koroteev et al. [15], the appearance of the Rashba splitting of the Au(111) surface state "came as surprise". It should be noted also that the splitting, estimated within the 2D electron gas model, was found to be by several orders of magnitude smaller than that observed in experiment [16], so that it was possible to state only a qualitative agreement with the theory.

In the systems with asymmetry with respect to the axis normal to the surface, Rashba splitting leads to the spin polarization of the bands within the surface plane. By analogy, it was suggested that, in the case of the Au(111)

surface, the asymmetry is brought about by the surface potential, in particular by the surface barrier. Then, for the Au(111), the twin surface states must show an opposite spin polarization, and several studies were performed to reveal the spin polarization of the surface bands of Au(111) by means of spin- and angle-resolved photoelectron spectroscopy [16]. However, as it was mentioned in [16], the spin polarization of the initial state (photohole) is not necessarily that of the photoelectron, in particular when the spin-orbit coupling is strong (like in the case of Au with $Z = 79$). Therefore, the interpretation of spin-resolved photoemission spectra can become complicated due to the various spin polarization effects.

Hence, while the splitting of the surface bands of Au(111) has been well established in a number of photoemission experiments, the commonly recognized interpretation of the splitting of the surface bands as a result of the spin-orbit coupling steel needs a better justification. Then, the cornerstone suggestion that a surface itself can cause the break of the symmetry has led to the generally accepted concept of the nature of the splitting of surface states of metal surfaces (see [8] for a recent review). This concept, however, has obvious shortcomings. First, any surface cannot be separated from the bulk and therefore cannot have its own symmetry. In other words, any surface-induced lowering of symmetry means the lowering of the symmetry of the net system, so that the symmetry of the interior cannot be considered separately. Second, any real crystal or film always has an opposite surface, which restores the inversion symmetry in a general case. It should be noted in this regard that the model of a semi-infinite crystal seems improper for the study of the spin-splitting of surface bands caused by SOC. Third, if the existence of a surface were sufficient to initiate the break of inversion symmetry, the Rashba-type spin-splitting would be observable for surface bands of all clean surfaces of all metals, while in fact there are only a few reports of the splitting for clean metal surfaces (e.g., for Ag(111) [14], Bi(111) [15], Cu(111) [17], Cu(110) [18], and W(110) [19]; for review, see [7–9]), which, because of biased determination of the spin polarization and actual surface conditions, might be interpreted differently, or for surfaces covered by adsorbed layers, which could destroy the inversion symmetry.

In the present paper, we revisit the interpretation of the twinning surface bands of the Au(111) surface, which has become a basis of subsequent interpretation of the bands of other metal surfaces, by means of fully relativistic (that is, with account for spin-orbit coupling) DFT calculations for the repeated-slab model. The calculations were performed with ABINIT [20] set of programs using Troullier-Martins [21] pseudopotentials and plane-wave decomposition of the wave functions. The LDA exchange-correlation potential was in the Goedecker-Teter-Hutter (GTH) form [22]. The cutoff energy of 24 Ha and $6 \times 6 \times 1$ lattice of k-points provided the adopted 0.001 Ha convergence of the energy. In the course of the standard structural optimization, the cutoff was decreased to 20 Ha and calculations were carried out within semirelativistic approximation (i.e., without SOC).

2. Results and Discussion

Figure 1 shows the band structures calculated for a 13-layer Au(111) film in both the semirelativistic and full relativistic approximations. The surface bands (marked red in Figure 1) appear in a doublet form already in scalar calculations, which means that the splitting seen in Figure 1(a) stems not from spin-orbit coupling but is a result of possible interaction of electrons in the surface states of the terminating surfaces, as it was suggested in [14]. Indeed, the spin-orbit interaction only slightly increases the estimated binding energies of the bands (the relativistic surface bands are shifted down by ~0.08 eV) but does not initiate the spin-splitting, so that each surface band in Figure 1(b) still contains 2 electrons with opposite spins.

It was suggested [14] that the split of the surface bands stems from the interaction between surface states of opposite faces of the slab, and since this split is significant, the spin-splitting, being noticeably smaller, is not revealed. Then, it was proposed to increase the number of layers (and thus the thickness of the model slab) to diminish the interaction between the Au(111) surfaces.

Results of the calculations for various thicknesses of the films confirm these suggestions (Figure 2). In particular, with increasing the thickness of the slab, the splitting of the surface bands noticeably decreases (from 0.170 eV at Γ for 11-layer slab) and, perfectly consistent with results of calculations in [14], for the 23-layer film becomes negligible (0.015 eV).

To facilitate comparison and discussion of obtained results, it is convenient to present the band structure, calculated for the 23-layer Au(111) slab, in the same scale as adopted by Nicolay et al. [14] (Figure 3).

It is evident from comparison of Figures 3(a) and 3(b) that the account for spin-orbit interaction results in a well-pronounced splitting of the bands, which seemingly remain degenerated at Γ point, just like it must be for Rashba splitting. It should be emphasized that the relativistic bands (including not only surface bands but also the bands originated by the interior), shown in Figure 3(b), are almost perfectly consistent with the bands presented in [14] (in particular, the binding energies at Γ, of ~0.50 eV, are the same). It is just this splitting of the surface bands that was interpreted as a Rashba-type spin-splitting, thus apparently supporting the concept of the brake of the inversion symmetry at the surface and hence the lifting of the spin degeneracy of the bands.

In fact, however, the splitting of the Au(111) surface bands seen in Figure 3(b) is found to be not the Rashba splitting. This conclusion directly follows from a detailed analysis of the bands using actual numerical values obtained in the relativistic calculations. Specifically, each surface band of the doublet is twice degenerated; that is, it contains 2 states with opposite spins, so that there are not 2 but 4 bands which form 2 spin-degenerated bands. Furthermore, these bands are not perfectly degenerated at Γ point but split by 0.011 eV, which is close to the value obtained in scalar-relativistic calculations (a quite similar splitting at Γ also can be revealed from Figure 1 in [14] by zooming).

In other words, there is no spin-splitting of the surface bands despite an evident similarity with Rashba effect, which

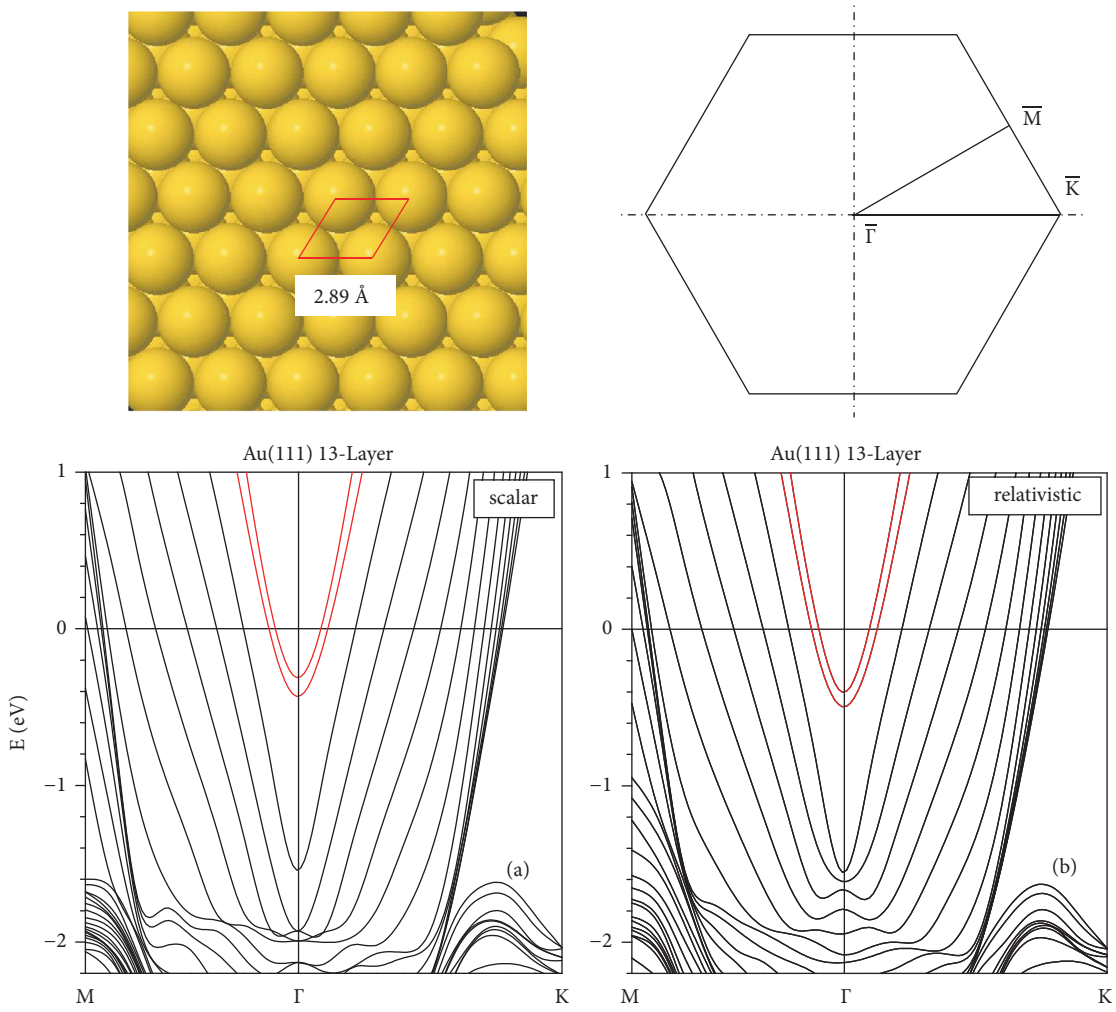

Figure 1: The band structure of Au(111) calculated for 13-layer film in the semirelativistic (a) and full relativistic (b) approximations. The surface bands are marked red.

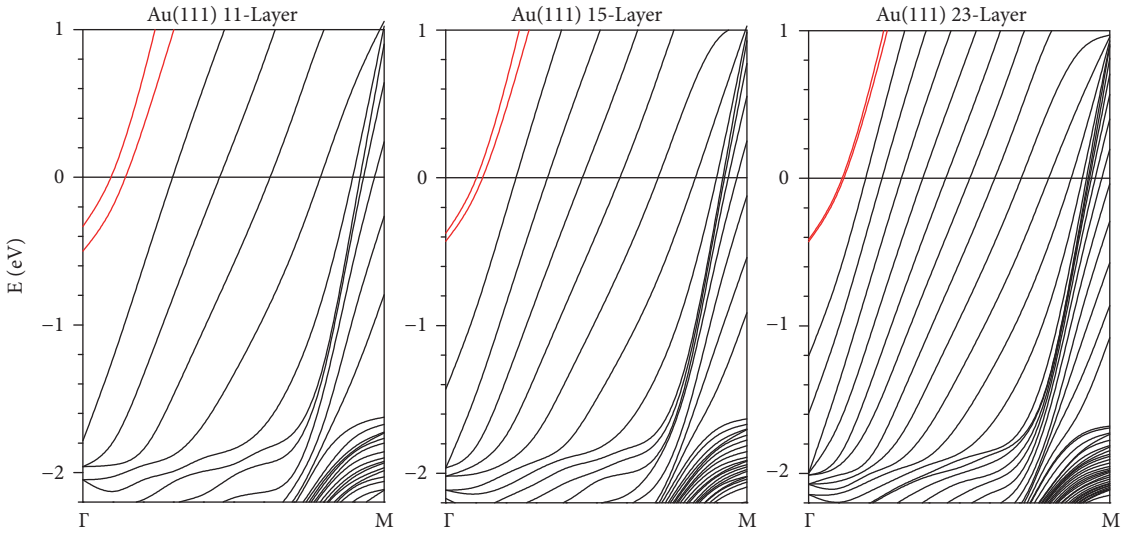

Figure 2: The band structure of Au(111) calculated for various thicknesses of films in semirelativistic approximation.

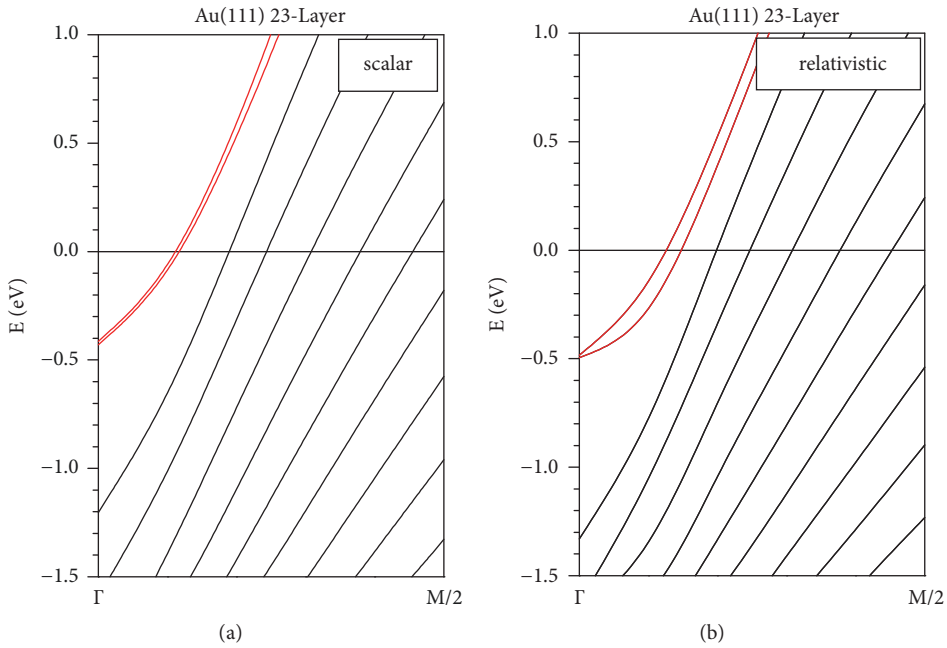

Figure 3: The band structure calculated for the 23-layer Au(111) slab in semirelativistic (a) and full relativistic (b) approximations.

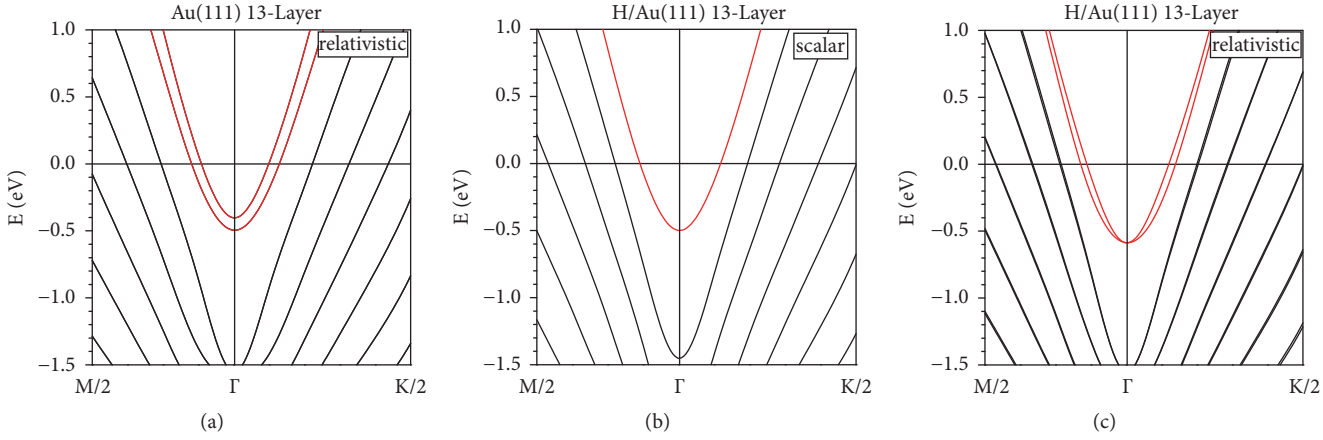

Figure 4: Band structures of the 13-layer Au(111) slab (a) and the slab with H overlayer (b, c), calculated in semirelativistic (b) and full relativistic (a, c) approximations.

here is apparent. The Rashba splitting could be switched on by breaking the inversion symmetry of the slab with a help of adsorbed layer, so we have calculated semirelativistic and relativistic band structures for Au(111) film with one surface covered by H (Figure 4) (similar method was adopted in [15], for Bi(111) films, to eliminate, as it was suggested, the interaction between surface states).

The twinning of surface bands of the 13-layer Au(111) film (Figure 4(a)) stems from the interaction between two faces of the slab [14], as noted above. Hydrogen adsorption on one surface of the slab leads to the coupling with the surface state and therefore only one of the parabolic surface bands, corresponding, as it is widely recognized [8–14], to the opposite (clean) Au(111) surface, remains in vicinity of E_F (Figure 4(b)). In contrast to the films with clean surfaces, the slab with one surface covered by adsorbate (hydrogen in the present case) has no inversion symmetry. Consequently, the SOC coupling lifts the spin degeneracy and causes the spin-splitting of the bands (Figure 4(c)). At Γ point, the bands are exactly degenerated, as it should be according to Kramers' degeneracy at $\mathbf{k} = 0$.

3. Conclusion

Results of present calculations of the band structures of Au(111) films lead to conclusion that the twinning of the surface bands, observed in photoemission experiment, does not necessarily correspond to the spin-splitting of the surface states caused by the break of the inversion symmetry at the surface. In calculations for thin Au(111) films, the twinning

can be obtained within nonrelativistic or scalar-relativistic approximation, but these surface bands are split in energy at Γ point. The energy gap between the bands decreases with increasing the film thickness and, for the 23-layer film, consistent with earlier findings [14], is essentially eliminated.

The account for spin-orbit interaction, in perfect agreement with calculations by Nicolay et al. [14], results in a well-pronounced splitting of the surface bands, which seemingly remain degenerated at Γ point. However, a detailed analysis of the bands, using actual numerical values obtained in the relativistic calculations, leads to conclusion that each surface band of the doublet is twice degenerated; that is, it contains two states with opposite spins. In other words, there is no spin-splitting of the surface bands despite an apparent similarity with Rashba effect. This result ultimately indicates that the existence of a surface itself is insufficient to remove the inversion symmetry of the system and thus to lift Kramers' degeneracy. The inversion symmetry can be eliminated by H overlayer adsorbed on one face of the Au(111) film, which leads to the appearance of the spin-splitting of the bands.

It should be stressed that these obtained results do not discard the possibility of creation of metal surfaces or adsorbed films having spin-split surface bands, but this effect ultimately requires the break of inversion symmetry, which can be accomplished either by interaction with the substrate or by adsorption, for example, of H monolayer.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The author declares that there are no conflicts of interest.

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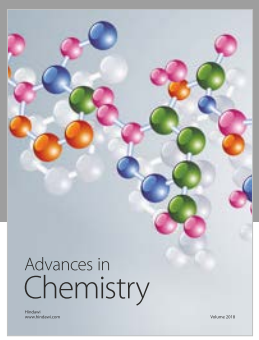

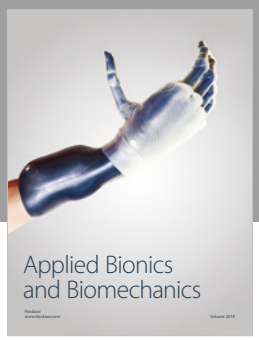

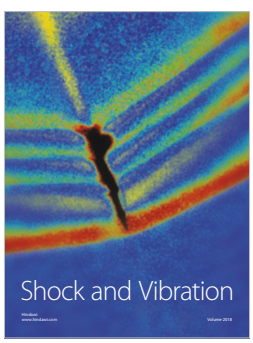

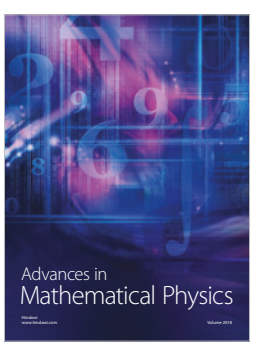

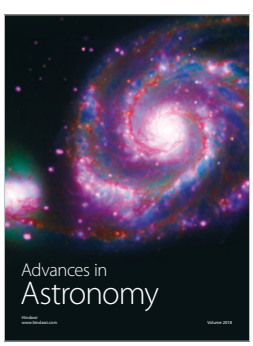

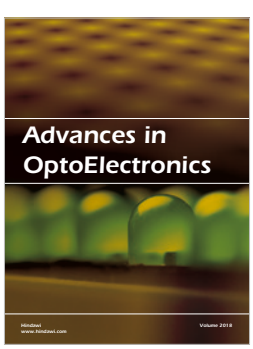

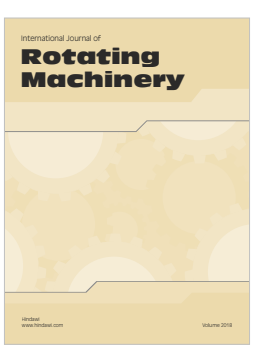

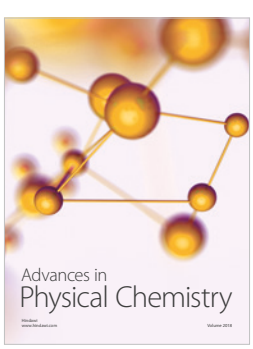

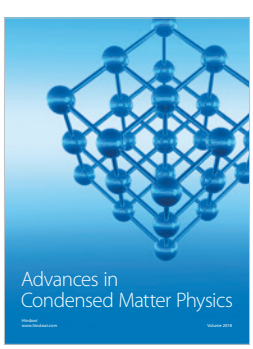

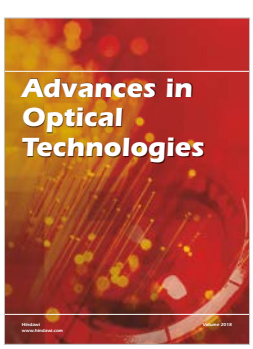

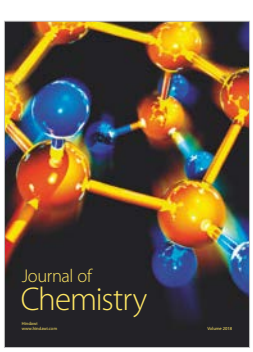

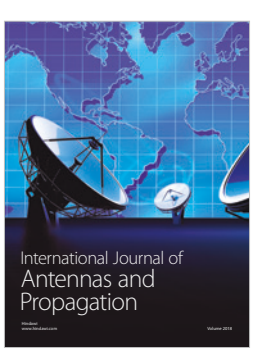

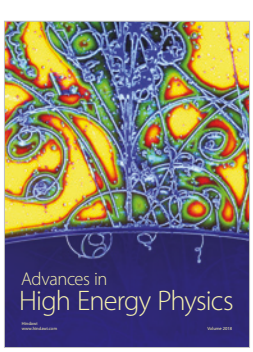

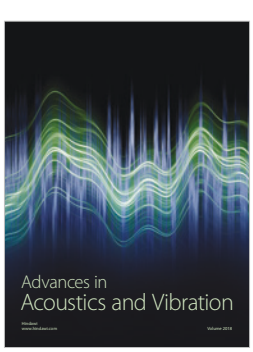

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