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Electronic surface states of beryllium, magnesium, zinc and cadmium

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We have projected the three dimensional energy bands of Be, Mg, Zn and Cd on to the two dimensional Brillouin zone of the 001 surfaces of these hexagonal close packed metals. The projections show fairly large band gaps at Γ for Be and Mg closing at points in the Γ–M and Γ–K directions inside the two dimensional Brillouin zone. Zn and Cd, however, do not have any band gap at Γ, they have very small band gaps inside the two dimensional Brillouin zone. From the study of these band gaps it is concluded that although Be and Mg have good possibility of having surface states, the probability of surface states in Zn and Cd is very small.

1. Introduction

The study of the electronic structure of surfaces dates back to 1930s with the pioneering work of Tamm (1932) and Shockley (1939). Since then it was neglected presumably because of the tremendous emphasis put on the electronic energy states of bulk materials. However, recently the problem is taken up and has since proceeded in two definite directions. The first approach is through the analysis of electron gas (Lang 1973) and the second approach is through the study of bulk band structures (Forestman & Heine 1970, Alldredge & Kleinman 1972, Caruthers *et al* 1973, 1974; Caruthers & Kleinman 1974, Dempsey *et al* 1975, 1976; Sohn *et al* 1976). The second approach have generally been concentrated on the study of the states whose energies fall in the gaps of the bulk material and whose wave functions are localized in the surface region. All these calculations lack self-consistency and is mainly of parametrized type (Caruthers & Kleinman 1974, Dempsey *et al* 1975, 1976; Sohn *et al* 1976) whose parameters are found out from the bulk calculations. Howevers, only recently some first principle methods have been put forward (Kohn 1975, Kar & Soven 1975) but detail self-consistent calculation with these methods are yet to be performed. Meanwhile a good insight in the surface states could be obtained by the studies of the band gaps of bulk materials. In fact Pendry & Gurman (1975) have recently obtained a new condition for the existence of surface states. They obtained that if the bulk crystal has a mirror plane parallel to the surface and a centre of symmetry, narrow gaps at centre and edges of the Brillouin zone may contain surface states. Another way of looking into the problem is to

project the three dimensional energy bands onto the two dimensional Brillouin zone. Unless one is specially interested in very thin films, the projection gives all the informations about the existence of surface states in the gaps. As the existence of energy gaps in the projected bands is the primary condition of the existence of surface states, the study of the energy gaps in different symmetry points and directions gives a fairly good insight in the study of their surface states. Upto now the study of the surface states of metals were mainly concentrated on the metals Li, Al, Cu and Fe in films of different crystallographic directions (Alldredge & Kleinman 1972, Caruthers *et al* 1973, 1974; Caruthers & Kleinman 1974, Dempsey *et al* 1975, 1976, Sohn *et al* 1976) But divalent hcp metals Be, Mg, Zn and Cd have got little attention although a large number of experimental and theoretical studies of the bulk electronic properties of these solids are available (Neddermeyer 1976, Holder and Alonso 1976, Shevchuck *et al* 1973, Tejida *et al* 1973, Townsend 1953, Falicov 1962, Loucks & Cutler 1964, Torrel 1966, Chatterjee & Sinha 1975, Sinha & Chatterjee 1977) Amongst these metals the most experimentally studied metal is Mg Although the earliest experiment of Townsend (1953) could not show any surface states, the experiments of Cardona (1973) did show a surface plasmon states just outside the valence band spectra of Mg In view of these experiments one would be interested to know the surface states of these metals from the theoretical point of view. In trying to do so one would have to take recourse to the heavy calculations by either the parametrized tight binding method of Caruthers *et al* (1976) or first principal calculation of Kohn or Soven (1975, 1975) Before embarking on such a huge calculation one can easily study the general features of the surface-states by studying the band gaps in the projected two dimensional energy bands of these metals. In this work we have obtained the 001 projected energy bands of these metals from bulk calculations of Chatterjee & Sinha (1975) The various energy gaps obtained in different symmetry points and axes of the two dimensional Brillouin zone are then discussed in the light of possible existence of surface states.

2. The Projected Bands

As the metals Be, Mg, Zn and Cd have hcp structure, both real and reciprocal lattice have the same hexagonal symmetry The unit cells in the real space and the reciprocal space have the shape of hexagonal prism as shown in figure 1 differing only in orientation and magnitude. Therefore, if we consider the 001 surface of these metals the two dimensional Brillouin zone of these metals will simply be the ΓKM plane of the three dimensional Brillouin zone and the two dimensional Brillouin zone would then look like as shown in figure 2. The symmetry points and axes would then be described by the triangle ΓKM. The projected bands along these triangle are shown in figures 3, 4, 5 and 6 for Be,

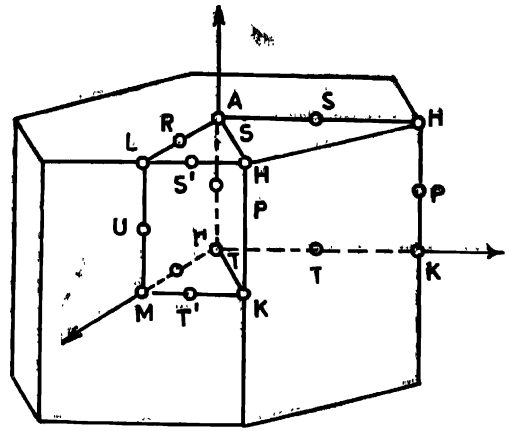

Fig. 1. Brillouin zone for the hexagonal Bravais lattice with symmetry points and axes following the notations of Herring

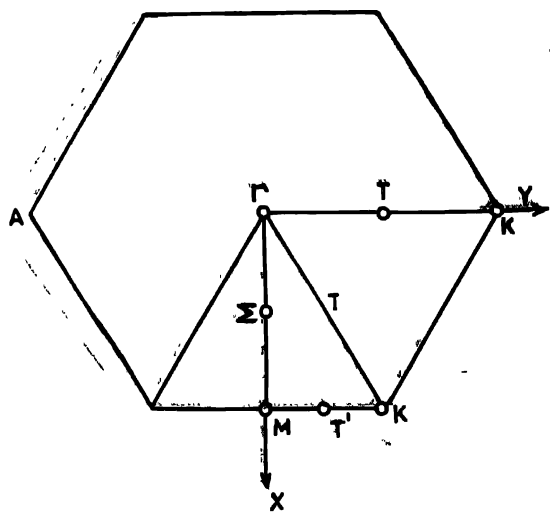

Fig. 2. Projected Brillouin zone in the (001) direction for the hexagonal Bravais lattice.

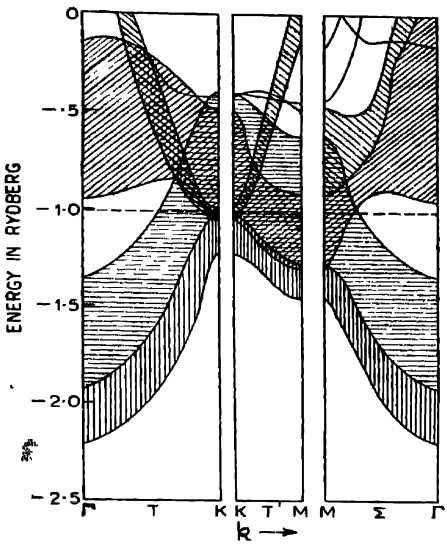

Fig. 3 (001) energy bands of Be.

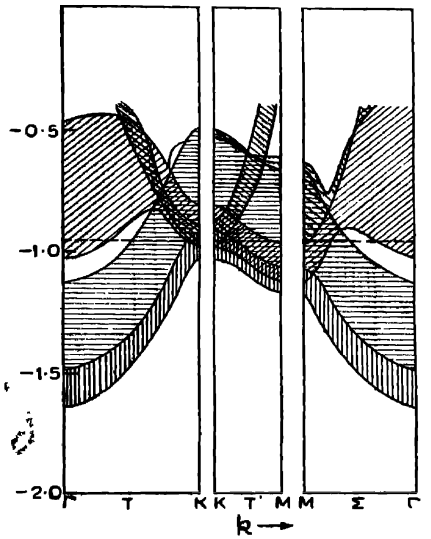

Fig. 4. (001) energy bands of Mg.

Mg, Zn and Cd respectively Since these are projected from bulk states, surface states can exist at a value of K where there is an energy gap in the projected band If we concentrate our attention to the origin of these gaps we notice that the Γ eigenvalues are projected from the (001)Δ direction of the three dimensional bands. Similarly at the point K, the eigenvalues are projected from the $3D$ bands along the line P. Because of the inherent degeneracy of the bulk states at A, H and at symmetry lines S there is no gap in the Γ–K direction between the first two valence bands. Similar situation exist in Γ–M direction where the points A, L and the symmetry line R has the same nature. The projected bands are thus connected in pairs and gaps occur only between two such pairs of projected bands. We now describe the projected bands and possible existence of surface states of these metals one by one From figure 3 it is quite evident that there is a large band gap at Γ and hence the possibility of surface states occurring in this gap is quite high The gap then decreases along the

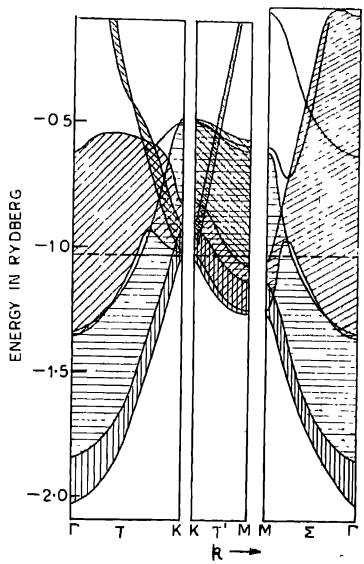

Fig. 5. (001) energy bands of Zn.

Γ–K line cutting the Fermi energy level at a K point 10/17th of the Γ–K line away from the Γ point, finally closing at a K point 10/15th of the Γ–K line away from the Γ point Similarly along the Γ–M direction the gap is largest at Γ and then closes at 10/14th of the Γ–M line away from Γ. The Fermi level also

intersects the gap almost at the same point. In the K–M direction, however, there is no gap and hence there is no possibility of surface states Next if we go on to figure 4 for Mg, we find that here also the gap is largest at Γ although the magnitude is much less than that of Be The gap decreases from Γ to zero at the point 10/15th of the Γ–K line and 10/15th of Γ–M line away from Γ. Here the Fermi line unlike Be do not fall in the gap near Γ point The Fermi line crosses the gap at the points 1/3th and 1/2th of Γ–K line and 10/27th and 10/17th

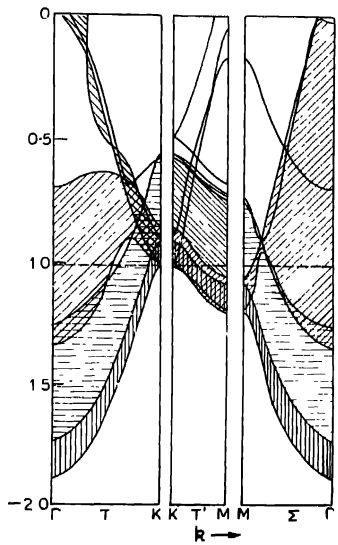

Fig 6. (001) energy bands of Cd.

of Γ–M line and has only limited region of K values The nature of the gaps in the next two metals Zn and Cd is quite different from that of Be and Mg Zn and Cd have no gap at Γ and only very small gaps exist in the Γ–K and Γ–M direction. The gap in the Γ–M direction of Cd is almost negligible. Although the Fermi line crosses these small gaps, there is only very small possibility of finding surface states experimentally considering the smallness of magnitude of the gaps.

4 Discussion

If we go through the figures 3, 4, 5 and 6, we find that the gap at Γ for all these metals decreases from Be to Mg, then overlapping for Zn and Cd, the overlapping being largest for Cd. Since the criteria of Gurman & Pendry (1975)

hold good for these metals one would generally expect surface states for all these metals inspite of the non-existence of band gaps at Γ point for Zn and Cd. However, considering the nature of the band gaps one may conclude that there is a high possibility of surface states for Be and Mg while the possibility of surface states for Zn and Cd being quite small

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