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Possible semiconducting properties of noble metal films

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Abstract. Energy states in thin metallic films are considered. For very thin films, these are confined to two-dimensional sheets in k -space. Within a sheet, it is possible for an energy gap to exist between successive zones. Under certain circumstances, this energy gap can persist in three dimensions, provided that the film is exactly two atomic planes thick. In a monovalent metal film that is just two atom planes thick, there are just sufficient electrons to occupy the first zone in the first sheet of states. Therefore, if the three-dimensional gap exists, the metal will be a semiconductor or an insulator. This possibility has been investigated for the noble metals copper, silver and gold. The outcome of the calculations depends on the assumptions made concerning the effective thickness and the depth of the potential well associated with the film. However the conclusion is reached that such a film of a noble metal will probably be semiconducting, provided it is oriented in the (111) direction. It seems unlikely that the required films can be produced with present experimental techniques. However, it should be possible to produce noble LUCS (or superlattices). Whether or not these are semiconducting cannot be predicted on a simple model.

1. Introduction

The purpose of this note is to point out the possibility that thin films of noble metals might become semiconductors, or insulators. The particular circumstances in which this could happen is that of a film oriented in the (111) plane, and exactly two atomic layers thick.

Wave functions for electrons in motion in a crystalline solid, in a direction in which it is finite, are formed from standing waves, with the relevant component of the k -vector positive (Guillemin and Uzan 1969, Cottey 1971, 1972a, b, 1973a, b, Messmer 1977, Bilek and Skala 1978). For a thin film, the allowed values of k therefore lie on sheets in k -space parallel to the film. As this becomes thinner, the distances between the sheets becomes larger, and the energies for motion perpendicular to it become more widely spaced. These quantum size effects have been observed experimentally by thickness-dependent conductivity oscillations, and by electron tunnelling spectroscopy in (for example) Pt (Fischer and Hoffmann 1980).

The present interest is in thin films of noble metals. It will be shown that there is likely to be an energy gap at the top of the s - p band for electron motion in the plane of the film. If, in addition, the lowest energy in the second sheet of states in k -space is greater than the highest energy in the s - p band in the first sheet of states, all of the electrons will condense onto the first sheet, completely filling the s - p band. The metal will now be a semiconductor or insulator.

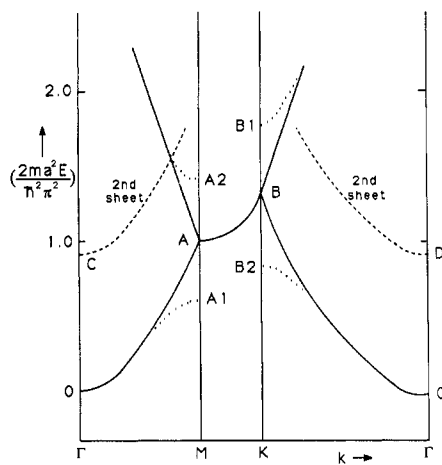


Figure 1. E - k curves: —, empty lattice (free electron) curves; ·····, modification due to lattice potential causes gaps A1 to A2 and B1 to B2; ----, second sheet of levels. The position of the lowest energy (C, D) has been calculated for an infinite well. This energy will vary according to the assumptions made (see text). The notation Γ MK is the same as that used by Sohn *et al* (1976). Γ refers to the zone centre, K to the points of the hexagonal zone, and M to the centre of the six sides of the zone.

2. The form of the energy bands

Consider a crystalline film of a noble metal, oriented parallel to the (111) face of the FCC bulk material, and assume it to consist of just two atomic planes. The structure will be hexagonal, since a minimum of three (111) layers are required to establish an FCC structure. Likewise, the two-dimensional Brillouin zone in the plane of the film will be hexagonal. To calculate the electron energy, it was assumed that an NFE picture can be applied to calculate the energy of motion in the two dimensions parallel to the film, and that the energy of motion perpendicular to the film has to be added to this. The latter was taken to be equal to one of the energy levels of a one-dimensional potential well, and to be dependent therefore on its width and depth. These energies are therefore the 'zero energies' of the successive sheets of states in k -space. The empty lattice bands, calculated in this way, are shown in figure 1, where the notation is the same as that of Sohn *et al* (1976). In this diagram, the well has been assumed to be square, and of infinite depth, whilst its width has been taken to be equal to the distance between two (111) layers plus twice the close-packed radius. As usual with the NFE model the effect of the lattice potential is to introduce energy gaps at the zone boundary, with the point at A splitting into A1 and A2, and that at B into B1 and B2. An estimate of the possible magnitudes of the gaps at A and B can be made using pseudopotential data, which have been gathered together by Cohen and Heine (1970) and presented in the form of theoretical curves as a function of wave-vector, drawn to go through theoretical points of Jacobs (1968). The authors also presented additional points, taken from optical measurements, or from the half gap found in band structure calculations. There is some disagreement between these points and the curves, so predictions based on the latter are subject to uncertainty. For the present problem, there were no direct calculations for the particular reciprocal lattice vectors required, so values of the pseudopotential

were taken from the theoretical curves (Cohen and Heine (1970), figures 62–64) for the relevant reciprocal vectors. Using this procedure, it was found that there was a two-dimensional energy gap in gold of between 2 eV and 2.5 eV, with larger gaps for copper and silver, whilst the three-dimensional gaps were around 1 eV for copper and gold, and around 0.6 eV for silver.

If the present procedure is followed with films of (001) orientation, a similar picture is obtained, with two modifications. The first is that the ratio of the lengths of the two vectors of high symmetry are different, leading to a higher energy at the point analogous to B (figure 1). The second is that the thickness of the two-atom layer is greater than for the (111) case. This leads to a lower energy for the second sheet of levels, and will most probably mean that there will be no energy gap in a two-atom-thick film oriented in this direction.

3. Discussion

The s–p valence band in bulk noble metals approximates to a NFE model, but with large energy gaps (see, e.g., Burdick 1963, Snow 1968, Eckhardt *et al* 1984). This picture breaks down around the middle of the band due to hybridisation with atomic d levels. However, the present arguments are concerned with the top of the valence band, and so are not affected by this. Additionally, the low energy dispersion of the d bands in the bulk material means that they will not interact with the s levels in the second sheet of states. The NFE model therefore appears to be sufficient for the present purpose, as far as motion parallel to the films is concerned. The analysis of the motion perpendicular to the films is, however, open to more uncertainty. Clearly, the lowest energy of the second sheet of levels is strongly dependent on the assumptions that are made as to the depth and the width of the well, and these factors therefore determine the existence or otherwise of an energy gap. Taking first the effect of introducing a finite potential, a more realistic well depth was estimated by adding the work function to the Fermi energy (measured from the bottom of the conduction band). Using values estimated in this manner for all three metals, it was found that the lowest energy of the second sheet of states was reduced to a value near the bottom of the energy gap arising in the first sheet. This would mean that the material was a semimetal, or a metal. However, the width of the well used so far is almost certainly too large, in view of the fact that it will be narrower near to the bottom. Accordingly, a further calculation was made with the depth of the well still finite, but with a width equal to the distance between the (111) planes plus half the distance between neighbouring atoms. This is probably a better assumption than the one originally used, but may be slightly too small. As a result of this change the lowest energy of the second sheet of states was now higher than the value found in the original calculation with the infinite well. Clearly the form and dimensions of the well are of critical importance. Further problems arise due to the fact that the potential variations within the well have been ignored. If, in fact, we are justified in expecting the states for a film just two layers thick to be Bloch functions, the component of the k -vector perpendicular to the film will be close to the Brillouin zone boundary, and the energy will be reduced by the depression of the E – k curve. Additionally, as indicated earlier, the accuracy of the pseudopotential is also extremely important. Whilst there is obviously a lot of uncertainty in the calculations, there appears to be quite a strong possibility of semiconducting behaviour.

Two other questions arise if experimental verification is considered. In the first place it would be necessary to be able to produce such layers, and in the second place they would need to have sufficient conductance to be measurable. As far as the second point is concerned, much will depend on the effect of the small dimensions on electron scattering. Since the films being considered would have sides that were perfect crystal planes, electron reflection at the boundary would be specular. Under these conditions, the effect of thinning the material should be small, and the bulk resistivity should be retained in very thin layers. This has been observed in CoSi_2 (Hensel *et al* 1985) for layers as thin as 200 Å, although for layers as thin as 125 Å, the resistivity has begun to rise. For the films under present consideration, the widths are considerably smaller than this and extrapolation is difficult. However, if the bulk resistivity is in fact retained, the sheet resistance of the present films would be about 15 to 20 $\Omega \square^{-1}$, which would be easily measurable. On the other hand, the onset of semiconducting properties would make measurements considerably more difficult. As far as the manufacture of films is concerned, the present evidence is uncertain, but appears unfavourable. Whilst very thin (oligatomic) films of metal have been made (Gradmann and Müller 1968a, b, Gradmann 1969), and even a monolayer (Abbati *et al* 1978), they have all been grown on metal substrates, making observations of conductivity difficult. Evaporation of metals onto insulators usually results initially in the formation of separate islands, which join together as the film becomes thicker. There is some very indirect evidence that some metals can form very thin continuous layers on graphite (Desrousseaux *et al* 1979), although their evidence for the only noble metal (silver) points against this possibility. Likewise, it appears that the initial growth of copper on graphite is in the form of islands (Egelhoff and Tibbetts 1979), whilst the initial deposition of all three noble metals on LiNbO_3 is also in the form of islands (Harnik *et al* 1985). Crittenden and Hoffman (1953) claimed to have made films of nickel as thin as 10.2 Å evaporated onto glass substrates. However, Neugebauer (1959) showed that such films made under rather better vacuum conditions probably consisted of small particles, and Crittenden and Hoffman's observations have been attributed to effects due to oxidation. The possibility of observing a two-layer noble metal film on an insulating substrate therefore seems rather small. However, it is possible to make layered ultrathin coherent structures (LUCS—or 'superlattices' in semiconductor jargon) of various metals (Schuller and Falco 1979, Gyorgy *et al* 1982, Shinjo *et al* 1983). Such a structure consisting of (say) alternate layers of silver and gold might result in an energy gap appearing that divides the states in the s-p band equally into two parts for motion perpendicular to the film, provided that the layers contained equal numbers of atomic planes. A three-dimensional energy gap is therefore a possibility in this type of structure, although for slightly different reasons. Whilst a metallic base would still be necessary, measurements could in this case be made of conduction perpendicular to the film. However, the possible energy levels in such a structure cannot be estimated even approximately by using a simple model.

The arguments presented above appear to apply also to the alkali metals. However, the small values of the pseudopotentials make the appearance of an energy gap unlikely. Additionally, these metals do not have a face-centred cubic structure.

4. Conclusions

There is a strong possibility that double (111) layers of noble metals have energy gaps above the s-p band, and then behave as insulators or semiconductors. It is uncertain

whether such films can be manufactured on insulating bases using present techniques. Noble metal LUCs could probably be manufactured, and may have interesting properties.

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