

On the Possible Role of Surface States in Optical Properties of Aluminium

A discussion of optical transitions in aluminium is given taking into account both interband and surface transitions. The absorption peak at 1.5 eV, originally interpreted as an interband transition corresponding to the Fourier coefficient V_{200} of the pseudopotential, is shown to overlap with another transition due to the existence of surface states on the (100) plane.

For the last several years the optical properties of aluminium have been studied by many workers. Optical constants (refractive index n and absorption coefficient k) have been determined within a wide spectral range ($\lambda \simeq 0.2$ – $30 \mu\text{m}$) [1–3]. In a publication by one of the present authors the optical constants of opaque polycrystalline aluminium films have been measured in the spectral region 0.4 – $2.5 \mu\text{m}$ [4] by using an ellipsometric method [5, 6]. The real and imaginary components of the complex dielectric constants $\epsilon^* = (n - ik)^2$ were plotted as a function of the wavelength λ and compared with DRUDE's free electron theory [7]. Drude's theory is valid only for large values of λ , since then the absorption of light is mainly due to free carriers. For shorter wavelengths, however, various transitions (e.g. interband) may take place. A detailed analysis of this problem has been given in [6, 8, 9]. Results of theoretical analysis of BRUST [9] predict the appearance of two interband transitions at the energies of 1.5 and 0.5 eV associated with Fourier coefficients of the pseudopotentials V_{200} , and V_{111} respectively. Only one strong peak in the spectral distribution of the absorption coefficient, observed at 1.5 eV was interpreted in [4, 9] as an interband transition. According to Brust, the peak at 0.5 eV could be overlapped by the free carrier absorption. As mentioned in [10], the optical constants of pure aluminium films are

highly sensitive to the presence of oxide coating and ambient atmosphere [11]. The influence of aluminium oxide and of adsorbed molecules is higher in the visible and ultraviolet regions than in the infrared. In [4, 6] a correction for the aluminium oxide layer has been done. A good agreement between the values of the optical constants after correction for Al_2O_3 and those determined in ultrahigh vacuum has been obtained [4, 10].

However, there exists also the possibility of another kind of transition than that discussed above. This transition can be due to the existence of localized surface states on metallic surfaces. In general, the surfaces of polyvalent and transition metals can exhibit localized states [12–15; 17–19] with energies lying in different regions of the energy spectrum with respect to the Fermi level [12]. They appear in narrow energy gaps which may be found in the energy spectrum of semi-infinite crystals of those materials. Obviously, in infinite crystals these narrow energy gaps are overlapped by global energy bands so that no effective global energy gaps appear. The above mentioned localized states being of the Shockley type are connected with the so-called inverted band gaps of the solid i.e. band gaps in which the ordering of the energy levels is inverted as compared with the situation of isolated atoms [16]. In semiconductors these inverted gaps lie mainly at the surface of the Brillouin zone. However, in polyvalent and transition metals they can appear inside the Brillouin zone, as shown in Fig. 1. Once a particular crystal surface is formed from an infinite

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crystal, surface states appear in the inverted band gaps related to that direction in the Brillouin zone which is perpendicular to the investigated crystal surface. The appearance of

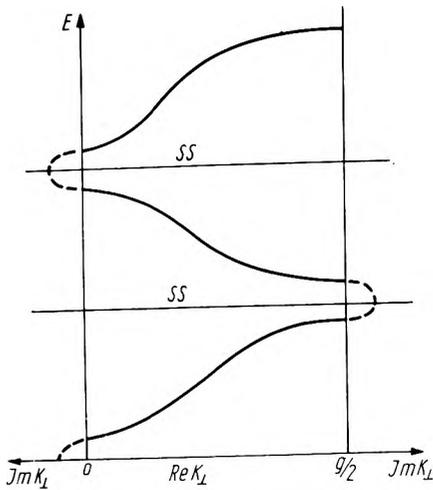


Fig. 1a

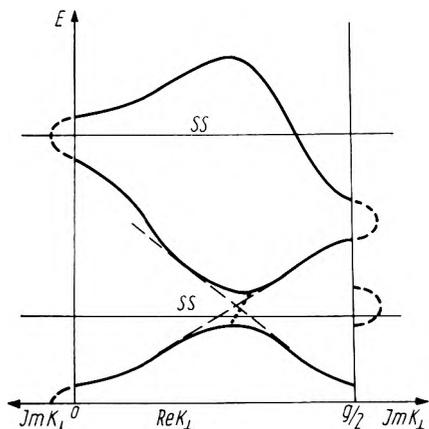


Fig. 1b

these states is associated with the interruption of bonds caused by the formation of the surface. The nature of Shockley surface states, as meant above, is most evident in the case of covalent crystals, for example Si, Ge and diamond [16]. However, even in polyvalent and transition metals, where the localization of bonds is by no means so well pronounced as in the case of covalent crystals, the above mentioned interpretation is still valid [12]. Surface states of this kind have recently been studied theoretically on different faces of transition and noble metals like Ni [17], Fe [12], W [18], and Cu [19]. As far as polyvalent metals are concerned only Al has been investigated [13-15]. Surface states have been found on the (100) surface of this crystal, where they form a band starting at

4 eV and extending down to 9.6 eV below the vacuum zero, which is taken here to be 15 eV above the crystal zero of energy [13]. The density of these surface states shows a large peak at 5.5 eV [13]. Assuming the work function of the (100) surface of aluminium to be about 4 eV, we see that this peak lies at about 1.5 eV below the Fermi energy (E_F). There exist also surface states on the (111) surface of aluminium as found by BOUDREAU [14]. These states form a band about 2 eV wide lying at a distance approximately equal to 3.3 eV below Fermi level. No surface states have been found theoretically on the (110) surface [14]. Since surface states on the both (100) and (111) surfaces of aluminium lie below the Fermi level, they are fully occupied.

In the case of (100) surface, an optical transition can be expected, caused mainly by the transition from the large peak of the density of states (at 1.5 eV below E_F) to the Fermi level. For the (111) surface, where the surface state density has not been calculated, one can expect optical transitions from the surface state band to the Fermi level. According to the results mentioned above, this could correspond to a peak lying somewhere between 3.3 and 6.6 eV. In this spectral region the measurements have been made on evaporated aluminium films by MENDLOWITZ [3]. As it is well known the (111) surface of Al is the least stable of the three most typical surfaces. Hence, it is not surprising that on such polycrystalline material no pronounced absorption peak has been found up to 6 eV.

It is interesting that the first of two optical transitions predicted theoretically, namely that at 1.5 eV, coincides with the peak observed experimentally for the same energy [4, 9, 13]. There is some discrepancy in the theoretical results obtained for the (100) surface in Refs [14] and [15], which is also mentioned by the respective authors. For this reason, and considering the fact that no relationship between the density of surface states and the energy can be found in [14] and [15], we refer here mainly to the work of Hoffstein. As mentioned above, the peak at 1.5 eV was originally interpreted as being due to interband transitions across the energy band, corresponding to the V_{200} Fourier component of the crystal potential. However, we see that this strong peak can be thought as due both to bulk and surface effects. According to what has been said about Ref. [3] it

seems to be no experimental evidence about the existence of the second peak predicted theoretically in the region 3.3–6.6 eV. In order to observe such surface transitions, experimental studies using monocrystalline materials and well defined surfaces should be extended to the spectral region of high energy.

Since Shockley localized surface states should exist in most polyvalent metals, further theoretical and experimental studies in this field are of a great importance.

Naturally, there exist also other methods of detecting surface states of the metals which should be combined with the measurements of the optical absorption. Among these methods we can mention field electron emission [20], photo-electron emission [21] and ion neutralization [22].

Influence possible des états de surface sur les propriétés optiques de l'aluminium

On a présenté les transitions optiques dans l'aluminium en tenant compte des transitions entre bandes ainsi que de celles de surface. On a prouvé qu'à 1,5 eV la crête d'absorption, considérée avant comme une transition entre bandes qui correspond au coefficient du pseudo-potentielle de Fourier V_{200} , se superpose à une autre transition due aux états de surface existant sur le plan (100).

О возможном влиянии поверхностных состояний на оптические свойства алюминия

Обсуждены оптические переходы в алюминии с учетом межполосных и поверхностных переходов. Показано, что пик поглощения при 1,5 eV, интерпретируемый раньше как межполосный переход, соответствующий коэффициенту Фурье псевдопотенциала, налагается с другим переходом, вызванным наличием поверхностных состояний в плоскости (100).

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