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THERMOREFLECTANCE OF TUNGSTEN FROM 0.3 TO 4.5 eV

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Résumé. — On présente le spectre de la réflectivité, modulée par la température, du tungstène de 0,3 à 4,5 eV. On interprète les structures en fonction de transitions directes, en bon accord qualitatif avec la structure des bandes électroniques. Des résultats, on estime le paramètre de couplage spin-orbite à 0,50 eV.

Abstract. — The thermoreflectance spectrum of tungsten is reported for the energy range of 0.3 to 4.5 eV. The observed structures are interpreted in terms of transitions in qualitative agreement with the calculated electronic band structure. The data yields a spin-orbit parameter of about 0.50 eV.

In this note we report optical measurements of the thermo-modulated reflectance of tungsten in the photon energy range from 0.3 to 4.5 eV. The electronic properties of tungsten (and of other b.c.c. transition metals, such as molybdenum) have been studied extensively over the last ten years because high purity single crystals are now available and most of the experimental techniques [1] have been applied to tungsten to study its electronic structure and the Fermi surface which are now quite well known. The experimental data obtained from anomalous skin effect measurements, magnetoacoustic effect, magneto-resistance, cyclotron resonance, de Haas-van-Alphen effect and radio-frequency size effect is well interpreted by a model devised by Lomer [2]. The electron *jack* surface, centered at the point Γ does not contact the hole octahedron centered at the point H as would predict a non relativistic energy band calculation. The two electron and hole surfaces are separated by a gap equal to approximately 8 % of the Γ H distance. This splitting is due to spin-orbit effects and from the separation between the two surfaces, the 5d spin-orbit parameter is estimated to be 0.4 eV. In order to interpret this vast amount of data, the electronic bands of tungsten have been calculated using the APW method by Mattheiss [3], Loucks [4], Petroff and Viswanathan [5] and more recently by Christensen and Feuerbacher (referred as CF) [6]. The early calculations aimed mainly at interpreting Fermi surface data while the last calculation made an extensive comparison of a calculated joint density of states with the optical work of Nomerovannaya *et al.*

(referred as NKN) in order to choose the *best potential*; with that potential they then interpreted the photo-emission experiments. However, there remain small discrepancies between the theory and the experimental results and these can be partially removed by optical measurements which provide the energy gaps between the bands and further define the electronic structure around the Fermi level. We will interpret our data guided by this CF calculation. At this point we remark that CF made a relativistic calculation, which leads to an energy dependent effective spin-orbit parameter, which gives results quantitatively different from those obtained by perturbation theory with an atomic energy independent spin-orbit parameter.

Thermomodulation techniques have been used with success in numerous studies of the noble metals since Scouler [7] studied gold in 1967, but few transition metals have been studied (only Ni [8] and Mo [9]). This technique is very sensitive to transitions involving bands at the Fermi level, since the temperature modulates the width of the Fermi distribution. The technique of temperature modulation that we have developed is quite easy to implant. We heat the sample by electron bombardment using approximately 5 W of a.c. power. We used different samples (bulk polycrystalline and rolled sheet of W) of about 100 μ electropolished down to 50 μ . The temperature of the sample can be varied from helium temperature to 500 K.

The optical properties of bulk polycrystalline samples of W have been studied by Roberts [10] in the visible and the near infrared, by Lenham and Treherne [11] in the visible and the infrared, by Junker *et al.* [12] between 2 and 24 eV and by Nomerovannaya *et al.* [13] between 0.06 and 4.9 eV. The last group also studied monocrystals (electropolished

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samples by ellipsometric techniques) as did Carroll and Melmed [14] (heat cleaned samples between 1.9 and 3.8 eV) and recently Weaver *et al.* [15] (unoriented crystals between 0.15 and 33 eV).

Nomerovannaya *et al.* [13] have observed different absorption bands : i) one from 0.3 to 0.6 eV with features at 0.33 and 0.4 eV, ii) a band from 0.6 to 1.2 eV with structures at 0.67, 0.92 and 1.07 eV, iii) a stronger and broader band from 1.2 to 6 eV with peaks at 1.7, 2.5 and 3.1 eV. The reflectivity experiments of Weaver *et al.* [15] are in qualitative agreement with these results, showing structures in the absorptivity at 0.43, 0.87, 1.57, 2.25, 3.06 and 4.3 eV which through a Kramers-Kronig analysis give structures at 0.42, 0.97, 1.82, 2.35 and 3.42 eV in ϵ_2 .

Our results are shown on figure 1, we give the $\Delta R/R$ spectrum of W at 77 K and room temperature. They are noticeable changes between the two in the infrared region, but below 77 K no real difference is observed, this is perhaps related to the fact that our modulation power is significant and that at helium temperatures we have a sizeable, but difficult to appreciate temperature shift.

FIG. 1. — Thermoreflectance of W near 77 K and room temperature.

The structures are well marked and in qualitative agreement with what was expected from the different band calculations and from the NKN [13] data. However, we are far from quantitative agreement. A comparison can be made with the partial joint density of states functions calculated by CF [6] for direct transitions between given initial and final energy bands, keeping in mind that thermal modulation spectra emphasize Fermi-level transitions which occur over an extended region of k space, and that complications arise from Fermi distribution broadening. Critical point transitions between parallel initial and final bands should also be observed. In order to clarify the discussion, we show in figure 2 the relevant bands taken from Christensen and Feuerbacher [6].

The low energy structures are associated with relativistic effects resulting in a splitting of the Δ_5 degeneracy and the removal of the Δ_7 crossings.

FIG. 2. — Energy bands along symmetry directions for tungsten, according to Christensen and Feuerbacher. The non-relativistic bands along Δ are also shown. The structures of the thermoreflectance spectrum are identified as direct transitions.

According to CF and NKN, the onset of interband transitions occur around 0.35 eV. We observed such a structure (marked A on the figures) at low temperature but it should not be very strong unless the Fermi level is not in the spin-orbit gap and there are undetected Δ_7 electron lenses.

The structure (B) around 0.55 eV comes from transitions between bands 3 and 4 around the Δ line [16]. These transitions yield an effective spin-orbit parameter ξ of 0.45 to 0.50 eV since they are related to the Δ_6 and Δ_7 states coming from the spin-orbit splitting Δ_5 . The temperature evolution of this structure clearly indicates Fermi level involvement.

The sharpest and strongest structure (C) occurs for energies in the range 0.70 to 0.85 eV, and this is associated with the onset of the broad bandwidth maxima at 0.92 and 1.07 eV observed by NKN. This structure could be attributed to the same band pairs as above i.e. (3.4) at G and (4.5) along Δ . Since most of these transitions do not involve the Fermi level, it would imply an important thermovariation of the d bandwidth, or more precisely a thermosensitivity of the splitting between Γ_7^+ and the upper Γ_8^+ . This explanation is not too plausible. We have here a sharp derivative like transition and it should involve the Fermi level and the only possible transition is at G between bands 3 and 4. If this

interpretation holds, it will be useful for a detailed comparison between theory and experiment. The bands involved are G_1 and G_3 . Introducing the spin-orbit coupling [17] opens the difference between the two new G_5 states by the amount of the spin-orbit parameter ξ . The onset of transition is at

$$G_5 - G_5(E_F) \approx G_1 - G_3(E_F) + \xi.$$

This is a region which is very sensitive to potential changes since E_F must be below N_1' (hole lenses) and below the minimum of G_1 since no electron pockets are observed there. (This interpretation rules out the one given by NKN for the structure they observed at 0.08 eV.)

The important signal (D) between 1.1 and 1.5 eV is more easily understood since there are numerous transitions from band 3 to the electron *jack*, and from it to band 5 in the Σ and Δ directions.

The next structures (E) with maxima at 1.85 and 2.2 eV come mostly from (4-5) and (3-5) transitions along Δ and from the hole lens at N to the next band. Along Δ there are three nearly parallel bands. Δ_6 and Δ_7 are spin-orbit split, optimistically these transi-

tions involving the Fermi level at Δ_6 and Δ_7 are seen (since they are more pronounced at 77 K) on the data around 1.75 and 2.30 eV in decent agreement with maxima in ϵ_2 found at 1.82 and 2.35 eV by Weaver *et al.* These transitions give again the same estimate of ξ .

The last important structure (F) between 3 and 4 eV does not involve transition to or from E_F but most certainly bands with critical points along Σ and around N .

The weak structure (G) around 2.7 eV should perhaps be related to (3-5) transitions around Γ and N . To end the description of the data, we add that we could not investigate below 0.30 eV and consequently we cannot confirm the surprising structure seen by NKN at 0.08 eV.

Satisfactory as it may seem, the agreement between the different optical data and the most recent and detailed calculation of CF is not very good. (This is also true for the Fermi surface data.) Difficult to interpret quantitatively, the modulation spectra of different kinds are complementary to the Fermi surface data and it is necessary to extend the theory away from the Fermi level, in order to obtain a more general description of the electronic structure of metals [18].

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