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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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On the Interpretation of the Emission Band L_{β_2} of Niobium

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In paper (1) the results were given of correcting the emission band L_{β_2} for the width of the level L_{111} and for instrumental distortion. The correction was carried out by the method proposed in paper (2). The purpose of the present communication is to interpret the corrected shape of the emission band, and also to clarify the character of the bonding forces.

Fig. 1

Figure 1 shows the corrected emission band L_{β_2} of niobium (curve I) and the experimental emission band L_{β_2} (curve II). The corrected emission band L_{β_2} has a complex character. In its long-wavelength part there is a considerable shoulder (A). Its short-wavelength part (B) ends with a sharp spectral boundary corresponding to the limiting Fermi energy.

In the outer shell of a free niobium atom there are 5 electrons (1 in an s-state and 4 in d-states). If all these 5 electrons were collectivized in solid niobium, then the width of the emission band would be determined, according to (3), by the relation

$$\Delta E\,(\mathrm{eV}) = \left(\frac{n}{0.00453\,V_a}\right)^{2/3}, \tag{1}$$

where n is the number of free electrons per atom; V_a is the volume per atom.

It follows from relation (1) that for $n = 5$ the width of the filled part of the band should be equal to 15.6 eV; however, the width will be such in the case when the collectivized electrons are located in the first Brillouin zone, and if the electrons fill more than one Brillouin zone, then the width of the filled part of the overlapping zones, for the same n, will in the general case prove to be greater than that calculated from formula (1). Meanwhile, the width measured from the corrected band L_{β_2} at its base is 12.1 eV, which is considerably smaller than the value 15.6 eV indicated above.

This gives grounds to consider that, of the 5 electrons in the outer shell of niobium, only part are collectivized. This conclusion is confirmed by data on the magnitude of the Hall coefficient in niobium ([4]). The sign of the Hall coefficient in niobium is positive. The conductivity of niobium is predominantly hole-like, with a small admixture of electron conductivity. Meanwhile, if one assumes that all 5 electrons of niobium are delocalized, then 2 of them fill the first Brillouin zone, and 3 must be in the second zone. The second Brillouin zone is filled by 8 electrons; therefore 3 electrons would fill only its smaller part. It follows from this that if all 5 electrons were delocalized, the conductivity of niobium should be electron-like. It is obvious that the conductivity can be hole-like only in the case when the electrons fill the greater part of the first Brillouin zone.

In accordance with this, we consider it possible to divide the emission band L_{β_2} into two parts:

1. B—the part of the band adjoining the short-wavelength edge of the spectrum. It is the spectrum of collectivized electrons.

2. A—the long-wavelength part of the band. It is the spectrum of noncollectivized electrons.

From the width of part B at its base one can calculate the number of collectivized electrons by formula (1). The number of collectivized electrons determined in this way proved to be equal to 1.1–1.3 electrons per atom. Since the first Brillouin zone in niobium is filled by 2 electrons per atom (body-centered cube), the data obtained mean that this zone in niobium is more than half filled and that, consequently, the nature of the conductivity in niobium must be predominantly hole-like, which agrees with the positive sign of the Hall coefficient. Using the value of the Hall constant for niobium and taking into account that the contribution of negative carriers to the conductivity of niobium is small ([4]), we obtain a concentration of positive carriers of 0.93 per atom, which agrees well with the data obtained by us from the shape of part B of the emission band L_{β_2}.

Thus, part B of the corrected emission band L_{β_2} of niobium represents radiation caused by transitions from the atomic levels L_{111} to levels of collectivized electrons. It is interesting to note that the intensity ratio of the line L_{α_1}, equal to 0.047, coincides with its value for atomic d-states (calculated for 1.1 electrons), given in ([5]).

Part A of the emission band L_{β_2} in Fig. 1 represents transitions from the levels L_{111} to the levels of bound electrons. There are 3.7–3.9 such electrons per atom. The ratio of the integral intensity of part A to the integral intensity of the line L_{α_1} is equal to 0.005, i.e., at least an order of magnitude smaller than what would occur if the wave functions of the states of the bound electrons were atomic wave functions of d-states. Such a sharp decrease in the intensity of part A of the emission band means that the state of the bound electrons differs strongly from the atomic d-state. We believe that these 3.7-3.9 electrons of niobium form a covalent bond between niobium atoms.

It should be noted that R. L. Barinskii and E. E. Vainshtein, in studying the absorption spectra of a number of covalent molybdenum compounds ([6]), observed a decrease in the intensity of the corresponding parts of the spectrum.

Conclusions. 1. Corrected emission bands make it possible, together with electrical and magnetic measurements, to refine the character of the interatomic bond.

2. The emission band of niobium consists of two parts corresponding to collectivized and noncollectivized electrons.
3. It has been established that in solid niobium 1.1–1.3 electrons per atom are collectivized, while the remaining "valence" electrons participate in the formation of a strong covalent bond.

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Note: Figure translations are in progress. See original paper for figures.