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X-RAY L-SPECTRA OF NIOBIUM IN NIOBIUM DIBORIDE,  
NITRIDE AND CARBIDE, AND THE NATURE OF THE BOND  
IN THESE COMPOUNDS

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English Pages: 8

SOURCE: Issledovaniya Po Zharoprochnym Splavam,  
Moskva, Vol. 6, 1960, pp. 169-173.

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Date 28 Aug. 19 61

# X-RAY L-SPECTRA OF NIOBIUM IN NIOBIUM DIBORIDE, NITRIDE AND CARBIDE, AND THE NATURE OF THE BOND IN THESE COMPOUNDS

by

M.I. Korsunskiy, Ya. Ye. Genkin

Fluorescent spectra of the L series of niobium in niobium diboride, nitride and carbide, were obtained with a fast x-ray spectrograph focused by the Johann method using a bent quartz crystal of  $R \approx 1000$  mm radius. A specially designed fluorescent x-ray tube with replaceable anodes was installed in the spectrograph. In order to achieve greater intensity of the characteristic radiation of the substance of the surface of the primary anode, the cathode beam was transmitted at a small glancing angle of  $\sim 28^\circ$ . Vacuum in the spectrograph was maintained while the tube was in operation by MM-1000 and MM-40 pumps at  $10^{-5}$  mm Hg. The primary and secondary anodes were cooled by tap water. The temperature of the secondary anode did not exceed  $25^\circ$ . The surface of the primary anode was of silver. The fluorescent L-spectra of niobium are excited by the characteristic radiation of the L-series of silver.

The  $L_{\alpha 1}$ ,  $L_{\alpha 2}$ ,  $L_{\beta 1}$ ,  $L_{\gamma 1}$ ,  $L_{\beta 2}$ ,  $L_{\beta 3}$ , and  $L_{\beta 4}$  lines of the L-series of niobium (attendant lines) were obtained, as well as a group of satellites/of  $L_{\alpha 1}$  and  $L_{\beta 1}$  lines of the substances studied. The spectrum radiographs were subjected to photometry on the MF-4 recording microphotometer.

Comparison of the spectrograms obtained shows that when niobium goes into a compound, changes in various portions of the spectrum are observed. The shape and intensity of various lines of the spectrum and of the satellites are observed. Figure 1 represents a comparison of the photomicrographs of sections of the  $L_{\beta 2} - K_{\alpha S}$  spectrum (on identical scales) of these compounds and of metallic niobium. The exposures selected were such that the  $L_{\beta 1}$  lines obtained were of identical intensity (14 hrs for niobium, up

to 16 hrs for niobium carbide and niobium nitride, and 17 hrs for niobium diboride).

As we see, pronounced changes in the shape and brightness of the  $L_{\beta 2}$  band occur.

In the case of pure niobium it takes on the form of a normal spectral line with an index of asymmetry of 1.4, while in the case of niobium carbide and niobium nitride it is a wide line with two humps. In the case of niobium diboride this band is sharply asymmetrical with a very flat decline on the short-wave ~~side~~ <sup>end</sup>.

In order to obtain a more precise understanding of the nature of the changes occurring in the  $L_{\beta 2}$  band, the photomicrographs of pure niobium were superimposed with those of the compounds. Inasmuch as the <sup>intensities</sup> ~~brightnesses~~ vary, the selection of the lines which must be ~~completely~~ <sup>is of importance</sup> ("base line") ~~is of the essence.~~ <sup>is of the essence.</sup> completely matched when the photomicrographs are superimposed ~~is of the essence.~~

~~upon the other~~ We believe that matching of the  $L_{\beta 4}$  line is most practicable in this situation.

When we proceed from consideration of niobium to that of its compounds, we observe

Fig.1 - Photomicrographs of Segments of the  $L_{\beta 2} - K_{\alpha} S$  Spectra of NbC(1), NbN(2), NbB<sub>2</sub>(3) and Nb(4)

a change in the states of the outermost electrons. As a consequence, there is some variation in the relative intensity of the lines representing transitions competing with the ( $L_{II} - N_{IV}$ ,  $L_{III} - N_V$ ) transitions. For this reason, the  $L_{\alpha 1}$ ,  $L_{\alpha 2}$ ,  $L_{\beta 1}$ ,  $L_{\beta 6}$  lines cannot be used as base lines.

Of the noncompeting transitions  $L_I - M_{II}$ ,  $L_I - M_{III}$  (lines  $L_{\beta 4}$  and  $L_{\beta 3}$  respectively), the  $L_{\beta 4}$  line is a transition between the innermost levels, as a consequence of which variations in the outermost shell should manifest themselves least strongly here. Therefore, matching of the spectra of niobium and its compounds was done on the basis of the  $L_{\beta 4}$  line.

Figure 2 presents a superposed segment of the spectrum of niobium and of its

Fig.2 - Superposed Segment of Spectrum of Niobium and  
its Nitride in the Region of the  $L_{\beta 2} - K_{\alpha S}$  Lines:

\_\_\_\_\_ NbN; - - - Nb

nitride in the region of the  $L_{\beta 2} - K_{\alpha S}$  lines. ~~XX~~ As we see, the lines match over their entire curvature for Nb and NbN, and the  $L_{\beta 3}$  line retains its form and varies insignificantly in ~~XX~~ intensity (7%).

The variations occurring in the  $L_{\beta 2}$  band differ in nature. The niobium  $L_{\beta 2}$  band in the NbN spectrum is completely inscribed in the lower portion of the curve of the band of pure niobium. The variation of the  $L_{\beta 2}$  band looks as though a portion thereof disappeared in the formation of the nitride (hatched on drawing). It should be observed that the greatest variation is experienced by the middle section of <sup>the</sup>  $L_{\beta 2}$  band.

Analogous matchings were performed for the Nb - NbC, Nb - NbB<sub>2</sub> photomicrographs. The matched portions of the  $L_{\beta 2}$  bands are shown in Fig.3a. As we see, in all of the compounds examined, the  $L_{\beta 2}$  bands fit into the lower portion of the curve of the emission band of pure niobium.

Thus, in the nitride, the carbide, and the boride, the variation in the  $L_{\beta 2}$  band

takes on the nature of disappearance of a portion of the emission band. In the carbide and nitride, it is primarily the central portion that disappears, and in the boride it is a part of the band, displaced somewhat to the shorter waves. Inasmuch as <sup>the</sup> emission band  $L_{\beta 2}$  is complex, affecting the distribution of the electrons in accordance with the  $N_{IV}$ ,  $N_V$  and  $O_I$  levels, variations of this kind may serve as witness to the fact that different states ( $d_{3/2}$ ,  $d_{5/2}$ , and  $s_{1/2}$ ) participate in the linkage in different ways in the various compounds.

Fig.3 - Matched Segments of Bands  $L_{\beta 2}$  (a) and  $L_{\gamma 1}$  (b) Compounds of Niobium and the  $L_{\beta 2}$  and  $L_{\gamma 1}$  Bands of Pure Niobium

The  $L_{\gamma 1}$  bands also undergo sharp changes. Figure 3b shows the superposed  $L_{\gamma 1}$  bands of niobium in compounds and in the pure form (as in the case of the  $L_{\beta 2}$  bands, the superposition was based on the identical intensity of the  $L_{\beta 4}$  lines). Here, too, the disappearance of parts of the  $L_{\gamma 1}$  band of niobium is observed.

Table 1  
Integral Intensities of the  $L_{\beta 2}$  and  $L_{\gamma 1}$  Bands with  
Equal Intensities of  $L_{\beta 4}$  Lines

a) Substance; b) Intensity of  $\beta_2$  line; c) Intensity of  $\gamma_1$  line; d) Niobium;  
e) Niobium nitride; f) Niobium carbide; g) Niobium diboride

Table 1 presents numbers descriptive of the variations in the  $L\beta_2$  and  $L\gamma_1$  bands of pure niobium and ~~XXX~~ compounds thereof.

Comparison~~s~~ of the disappearing portions of the  $L\beta_2$  and  $L\gamma_1$  bands are made in Fig. 4, which also shows the curvature of the  $L\beta_2$  and  $L\gamma_1$  bands of pure niobium. The shape of the crosshatched section is the difference between the spectral intensities of the  $L\beta_2$  and  $L\gamma_1$  bands of pure niobium and the corresponding compounds.

Table 2 presents the measured integral intensities of the L series lines of niobium and its compounds. As we see, the ratio of the integral intensities  $I\beta_1/I\alpha_1$  varies. This bears witness to the redistribution of states in the fourth d-band (Bibl. 8).

In the spectra<sup>M</sup> of all the substances investigated, the  $L\alpha_1$  line is accompanied by numerous satellites representing the radiation of ~~twice~~<sup>doubly</sup> ionized atoms.

Table 2

a) Intensity; b) Niobium; c) Niobium ~~XXXXXX~~<sup>nitride;</sup> d) Niobium carbide; e) Niobium diboride

The distribution of intensities among the satellites of  $L\alpha_1$  of niobium and its compounds varies. Whereas the intensities of all the satellites vary ~~slightly~~ insignificantly, the intensity of the satellite of  $L\alpha_3$ , representing the  $L_{III} - M_V$  transition in the absence of ~~XX~~<sup>the</sup> one of the d-electrons of N-shell undergoes significant variation. The relative intensity of this satellite ~~XXXXXXXXXXXXXXXXXXXX~~ of all the niobium compounds mentioned is less than that of pure niobium. A reduction in the intensity of this satellite is particularly marked in the spectrum of  $NbB_2$ .



The reduction in the relative intensity of satellite  $L_{\beta 3}$  as we proceed to ~~XXXXXXXXXX~~ consideration of compounds confirms the conclusion previously arrived at to the effect that a portion of the electrons leave the d-band when niobium enters into compounds with carbon, nitrogen, and boron.

Fig.4 - Comparison of the Disappearing Portions of the  $L_{\beta 2}$  (a) and  $L_{\gamma 1}$  (b) Bands of Niobium in Compounds Relative to the Same Bands in Pure Niobium

As we see from Fig.3 the shape of  $L_{\beta 2}$  and  $L_{\gamma 1}$  lines of the nitride and the carbide is virtually identical and differs from the diboride lines.

This may indicate that in the carbide and the nitride, niobium atoms participate in a ~~linkage~~ <sup>coupling</sup> with ~~the aid of~~ <sup>the aid of</sup> electrons in identical states. As indicated, a pronounced diminution in the brightness of the  $L_{\beta 2}$  and  $L_{\gamma 1}$  bands is observed. This variation in line self-absorption. intensity may in part be due to ~~XXXXXXXXXX~~ However, inasmuch as ~~no~~ no shift of levels is observed, the rise in self-absorption when compared to that ~~XXXXXX~~ of pure niobium is something that may occur only as a consequence of the reduction in the degree of 4d orbits. filling of the ~~XXXXXXXXXX~~ The considerable reduction in the relative intensities of 4d orbits the  $L_{\beta 2}$  and  $L_{\gamma 1}$  bands, thus bears witness to the fact that a portion of the ~~XXXXXXXXXX~~ undergo coupling in ~~XXXXXXXXXX~~ all the compounds studied.

Consequently, the hypothesis that a portion of the ~~valence~~ <sup>valence</sup> electrons of nonmetallic shifts into the atoms ~~XXXXXXXXXX~~ deeper d-band of the metallic atom in the crystal when

interstitial

XXXXXXXXXXXXXXXXX phases of transition elements are formed, is not confirmed for

the carbides, nitrides, and diborides of niobium (Bibl.1, 2, 3, 4, 5). On the contrary, a comparison of the  $L_{\beta_2}$  lines of  $NbB_2$ ,  $NbN$ ,  $NbC$ , and  $Nb$  shows that the "defect" of this band declines monotonically from the boride to the nitride in accordance with the change in the number of vacancies in the 2p-shell of the interstitial atoms. This is in agreement with the conclusions drawn in (Bibl.6, 7), in which it is pointed out that in the bonds ~~XX~~ molybdenum carbide and titanium nitrides, as distinct from the hydrides, comes about not by the filling of empty ~~d-orbits~~ <sup>d-orbits</sup>, but by the transition of a portion of the d-electrons from the metallic atom into the bond.

The appearance of ~~humps~~ <sup>humps</sup> on the emission band may well be a consequence of the fact that the niobium atoms in these compounds have various configurations and that more electrons go into the linkage in certain atoms, and fewer in others, inasmuch as when we proceed from niobium to the carbide, nitride, and diboride, we have an increase in the intensity of  $I_{\beta_1}/I_{\alpha_1}$  (see Table 2) and it would therefore appear that in these compounds there is a corresponding increase in the  $\frac{n_V}{n_{IV}}$ , i.e., it is chiefly electrons in the  $d_{3/2}$  state that participate in this bond (Bibl.8).

#### Summary

1. The spectral lines of the fluorescent L-spectrum of niobium in the compounds  $NbN$ ,  $NbC$ ,  $NbB_2$  and in pure niobium have been determined.
2. The intensity and shape of the  $L_{\alpha_1}$ ,  $L_{\beta_1}$ ,  $L_{\beta_3}$ ,  $L_{\beta_4}$  lines varies insignificantly, whereas the intensity and shape of the  $L_{\beta_2}$  and  $L_{\gamma_1}$  bands undergo sharp changes.
3. The  $L_{\beta_2}$  and  $L_{\gamma_1}$  bands of niobium in the compounds prove to be only a portion of the corresponding bands of pure niobium.
4. The "truncation" of portions of the ~~XX~~ bands is a consequence of the fact that a portion of the electrons leaves the ~~d-orbits~~ <sup>d-orbits</sup>.

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McL-1019/1

5. In the formation of niobium nitride, carbide, and diboride, 4d-electrons leave the niobium atom to go into the linkage.

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MCL-1019/1