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I. B. BOROVSKII, V. I. MATYSKIN

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**Abstract**

**Full Text**

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**PHYSICS**

I. B. BOROVSKII, V. I. MATYSKIN

## **ORIENTATION DEPENDENCE OF THE LINE PARAMETERS OF THE CHARACTERISTIC X-RAY SPECTRUM OF ATOMS OF ELEMENTS IN SINGLE CRYSTALS**

### **BASIC PARAMETERS OF THE LINES OF THE $K$ - AND $L$ -SERIES OF V IN A SINGLE CRYSTAL OF $V_2O_5$**

*(Presented by Academician A. M. Prokhorov, October 2, 1969)*

From the theory of radiation and from the experimental data obtained up to the present time, it follows that the characteristic X-ray radiation of atoms of elements is distributed isotropically in space (for atoms in the free state and for those entering into solid polycrystalline compounds).

Our work is devoted to investigations of the parameters of the lines of the characteristic X-ray spectrum: the spectral position of the intensity maximum, the line intensity at the maximum, its width, and the asymmetry index, as functions of the direction of emergence of the radiation relative to the crystallographic axes in single crystals of low symmetry (spatial anisotropy; orientation dependence), i.e., to a study of the angular dependence of the line parameters when a single crystal serves as the movable anode of an X-ray tube. Independently of our work, preliminary results of investigations of the spatial anisotropy of fluorescent X-ray radiation excited in single-crystal specimens of  $FeCO_3$  and  $Fe_2O_3$  are given in <sup>(1)</sup>.

In the optical region, in the radiation-energy interval from 0.1 to 11 eV, the reflection method with polarized radiation from single crystals of low symmetry has shown a sharp influence of the anisotropy of the crystal lattice on the optical constants  $n$  and  $\chi$  <sup>(2)</sup>.

For the short-wavelength fine structure of X-ray absorption spectra, both experimentally and theoretically, a dependence of this structure on the mutual orientation of the polarization vector of the incident radiation and the crystallographic axes has also been shown <sup>(3-11)</sup>.

In the present communication we give the results on the orientation dependence of the lines of the  $K$ - and  $L$ -X-ray spectra of vanadium in a single crystal of  $V_2O_5$ \*. A positive orientation effect was also obtained by us for single crystals of zinc and graphite (in the latter case on a strongly textured polycrystal).

Vanadium pentoxide belongs to crystals of the rhombic system (space group  $D_{2h}^{13}-P_{mnm}$ ; unit-cell parameters  $a = 11.48 \text{ \AA}$ ,  $b = 4.36 \text{ \AA}$ ,  $c = 3.55 \text{ \AA}$ ).

The specimens were cut from a single crystal in the form of plates so that the tetragonal axis  $a$  lay in the plane of the plate. The plate was fastened in a special holder in which it could rotate in a plane perpendicular to the electron beam through  $360^\circ$ ; thus, the conditions

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the interaction of the electrons with the substance did not change when the single crystal was rotated.\*

The investigations were carried out on an MS-46 apparatus, on a spectrometer with a bent quartz crystal (planes  $(11\bar{2}0)$ ); the bending radius of the crystal was 250 mm; the resolving power was 4000. To study the lines of the  $L$ -series, a spectrometer with a lead stearate crystal was used as the analyzer. The radiation emerging at an angle of  $18^\circ$  to the plane of the polished surface was recorded with a proportional flow counter.

Part of the measurements of the line parameters was carried out not only for two mutually perpendicular directions (parallel and perpendicular to the  $a$  axis) of the radiation output, but also in the interval between them, in steps of  $15^\circ$ .

For each position of the specimen, the measured quantities of the line were its wavelength and its intensity at the maximum. Where possible, the line width at half-height and the asymmetry index were also measured.

The intensity at the maximum was measured at no fewer than 10 different points on the specimen for each "angular" position of the latter, and at each point more than  $1 \cdot 10^4$  pulses were accumulated.

To determine the spectral position of the line and other parameters, the latter, together with reference lines, was recorded from 20 to 80 times on the tape of an electronic potentiometer for each orientation, for different regions of the specimen, both with the single crystal stationary and with continuous displacement of the single crystal relative to the beam.

Fig. 1 Fig. 2

**Fig. 1.** Angular dependence of the parameters of the vanadium  $K\beta_{1,3}$ -line. The angle  $0^\circ$  corresponds to the direction parallel to the  $a$  axis.  $a$  —relative intensity  $I^\varphi/I^0$ ;  $b$  —spectral position relative to the reference line  $\Delta E$ ;  $c$  —line width at half-height  $\Delta$

**Fig. 2.** Shape of the  $VK\beta_{1,3}$ -line and its components (explanations in the text)

The measurement results are given in Table 1 and in Fig. 1. For all lines except the  $K\beta''$ -satellite, the intensity, on going from the direction parallel to the  $a$  axis to the direction perpendicular to it, decreases by 8-12%, while the displacement of the line maximum occurs toward the long-wavelength side. The width of the  $K\beta_{1,3}$  line increases in this case, and the asymmetry index decreases. Analogous measurements of the parameters of the  $K\beta_{1,3}$ -line were carried out on a plate whose surface was perpendicular to the  $a$  axis. In this case, upon rotation of the specimen no changes in the parameters under study could be observed. Their values proved to coincide with those for an angle of  $75^\circ$ , when the  $a$  axis lay in the plane of the polished surface.

\* This condition had to be observed because the integral intensity of the electron-excited x-ray radiation is itself orientation-dependent, which is associated with interference of the electrons and their channeling (<sup>12,13</sup>).

A satisfactory qualitative explanation of the established orientational dependence can be obtained by assuming that the crystal field causes splitting of the corresponding levels of vanadium atoms into the  $x$ -,  $y$ -, and  $z$ -components (we assume that the  $z$  axis is parallel to the  $a$  axis). Then radiation with a wave vector parallel to the  $a$  axis is emitted only in  $np_{x,y} \rightarrow 1s$  ( $3d_{x,y} \rightarrow 2p$  for  $VL\alpha_{1,2}$ ) transitions, whereas in the direction perpendicular to the  $a$  axis, the transitions  $np_z \rightarrow 1s$  make a comparable contribution. In the first case the line is formed from two almost isoenergetic components,  $x$  and  $y$ , and therefore it has the greatest intensity and the minimum half-width.

**Table 1**

Vanadium line	Reference line	Measured parameter	Direction of radiation emergence    to axis $a$	Direction of radiation emergence $\perp$ to axis $a$	Relative displacement, eV	Spectral position in the pure metal,* eV	Magnitude of chemical shift, eV
$VK\beta_5$	$CeL\beta_6$	Spectral position, eV	$26.7 \pm 0.3$	$26.2 \pm 0.3$	-0.5	29.5	-3.1
$VK\beta_5$	$CeL\beta_6$	Relative intensity	1	$0.92 \pm 0.01$			
$VK\beta_{1,3}$	$CrK\alpha_1$	Spectral position, eV	$12.3 \pm 0.1$	$11.9 \pm 0.2$	-0.4	12.6	-0.47

Vanadium line	Reference line	Measured parameter	Direction of radiation emergence    to axis <i>a</i>	Direction of radiation emergence ⊥ to axis <i>a</i>	Relative dis- place- ment, eV	Spectral position in the pure metal,* eV	Magnitude of chem- ical shift, eV
$VK\beta_{1,3}$	$CrK\alpha_1$	Relative inten- sity	1	$0.9 \pm 0.01$			
$VLa_{1,2}$	$MnL_1$	Spectral posi- tion, eV	$46.4 \pm 0.3$	$45.7 \pm 0.2$	-0.7	45.0	-0.9
$VLa_{1,2}$	$MnL_1$	Relative inten- sity	—	—			
$VK\beta''$	$VK\beta_5^{\text{met}}$	Spectral posi- tion, eV	$17.2 \pm 0.2$	$17.2 \pm 0.2$	0	$14.5 \div 16.9$	—
$VK\beta''$	$VK\beta_5^{\text{met}}$	Relative inten- sity	1	$1.5 \pm 0.1$			

\* Data of other authors.

When the direction of emergence of the radiation from the crystal is changed, a displaced  $z$ -component is added; its contribution grows as the direction perpendicular to the  $a$  axis is approached. In this case the “weight” of the original components decreases, and the line formed by the  $x$ -,  $y$ -, and  $z$ -components broadens, while the magnitude of the maximum intensity falls. Figure 2 gives the experimental curve for  $VK\beta_{1,3}$ , resolved into components on the basis of the adopted explanation of the orientational effect.

Curves 1 and 2 represent the distribution of intensity in the line over frequencies when the radiation emerges, respectively, parallel and perpendicular to the  $a$  axis. Curve 3 was obtained by dividing the corresponding ordinates of curve 1 in half and, according to the proposed scheme, depicts the line due to the  $1s \rightarrow 3p_{x,y}$  transition. Line 4 was obtained by graphical subtraction of curve 3 from curve 2 and, consequently, corresponds to the transition  $1s \rightarrow 3p_z$ .

The lines  $K\beta_{1,3}$ ,  $K\beta_5$ , and  $La_{1,2}$  are due to the electronic transitions  $3p \rightarrow 1s$ ,  $4p3d \rightarrow 1s$ , and  $3d \rightarrow 2p$ , respectively. The satellite  $K\beta''$ , as shown in [14], reflects the position of the low-energy bands of the crystal, whose state is

described predominantly by  $2s$ -wave functions of the metalloid. The spectral position of the maximum of  $K\beta''$  does not shift when the ...

of the exit direction, while the intensity ratio  $(IK\beta'')_{\perp}$  to  $[IK\beta'']_{\parallel}$  is 1.5.\* Such behavior of the  $K\beta''$  line, in our view, confirms the assumption stated above concerning the scheme of the orientational dependence, as well as the hypothesis regarding the nature of the origin of this satellite.

Studies of the orientational dependence of the parameters of characteristic X-ray spectral lines, caused by the polarization properties of transitions, are of interest because they make it possible to obtain information on the splitting of electronic levels in the field of the crystal lattice and data on the magnitude of this field; the information obtained may also prove useful for a more correct construction of electron wave functions in crystals. The existence of an orientational dependence of the spectral position and intensity of characteristic X-ray spectral lines must be taken into account (as must the spatial anisotropy of intensity caused by interference effects) in the practice of quantitative local X-ray spectral analysis, in which the regions analyzed are, as a rule, microscopic single crystals ( $1-10 \mu^2$ ) with different orientations of their axes relative to the direction of exit of the X-ray radiation.

A. A. Baikov Institute of Metallurgy Academy of Sciences of the USSR Moscow

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\* To determine the relative position and intensity of the line, a graphical subtraction was performed of the "tail" of the  $K\beta_{1,3}$  line (by a smooth continuation of its intense portion), which includes the  $K\beta''$  and  $K\beta_5$  lines.

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

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