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X-Ray Ultrasoft Spectra of Vanadium in Vanadium Oxides

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The Lα-emission spectra of vanadium in oxides V_2O_3, VO_2, V_2O_5, V_3O_5, V_4O_7, V_6O_{11}, V_6O_{13}, and V_3O_7 are investigated. It is discovered that the charge fluctuations in V_3O_5, V_4O_7, and V_6O_{11} have a period greater than the $2p_{3/2}$ hole life-time ($\sim 10^{-15}$ sec), while in V_6O_{13} and V_3O_7 this period is less than 10^{-15} sec.

For the last few years the interest of investigators in the vanadium oxides with mixed valency has risen markedly. It is due, first of all, to the temperature phase transition semiconductor-metal which almost all these oxides undergo, and which is accompanied by a jump of magnetic susceptibility and electric conductivity (*1–3*). In this connection, a question about the state of oxidation of vanadium atoms in intermediate oxides is of most interest. To study this question we obtained Lα-spectra of vanadium (2*p*–3*d*4*s* transition) in basic oxides V_2O_3, VO_2, V_2O_5 and in intermediate oxides V_3O_5, V_4O_7, V_6O_{11}, V_6O_{13}, and V_3O_7. Vanadium Lα-spectra of intermediate oxides are obtained for the first time. The spectra of basic oxides have been investigated formerly (*4*, *5*), and here are obtained anew for methodical purposes. Earlier we have investigated the $K\beta''\beta_5$-spectra of vanadium in the same compounds (*6*)

Specimens to be studied were prepared from highly pure vanadium pentaoxide and metallic vanadium in powder form. Vanadium trioxide V_2O_3 was synthesized by reduction of pentaoxide in the hydrogen atmosphere under the temperature of 600°C with subsequent annealing at 850°C during 10 hr. Vanadium dioxide VO_2 was obtained by heating the mixture of V_2O_3 and V_2O_5 taken in stoichiometric proportion in the evacuated quartz vessel at temperatures of 600 and 850°C during the periods of 5 and 30 hr, respectively. For the preparation of V_3O_5, V_4O_7, and V_6O_{11} bricketted stoichiometric mixtures of V_2O_3 and VO_2 were used, their synthesis being carried out in the vacuum $<10^{-3}$ torr at 1000°C. V_6O_{13} and V_3O_7 were obtained by annealing the bricketted mixtures of VO_2 and V_2O_5 at 660°C during 30 hr. The composition of basic oxides V_2O_3 and VO_2 was checked by chemical analysis. X-ray structure examination of the specimens was made using CuKα radiation. The measurements of reflection angles are in agreement with the data of literature (*7–9*).

Lα-emission x-ray spectra of vanadium are obtained by electronic excitation on the RSM-500 spectrometer (grating radius 6 m, 600 lines/mm). The value of apparatus distortion was 1.3 eV. X-ray tube conditions were chosen to give the most counting rate and at the same time to exclude decay of the sample material, and were $U = 3.6$–4.0 kV, $I = 2$–3 mA. During exposure time the sample temperature was not measured, however, indirect data suggest it was in the range of 200 to

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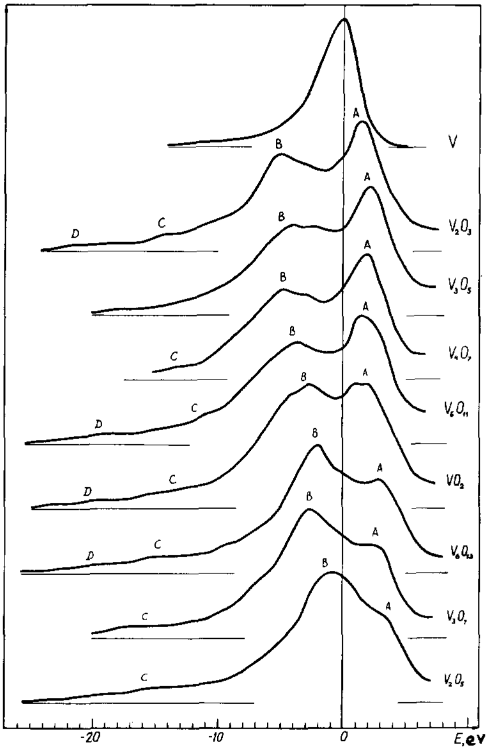

FIG. 1. X-ray Lα-emission bands of vanadium in oxides.

300°C. Thus, measurements were carried out in the metallic state of both V_2O_5 (T_c ~ 70°C), and V_3O_5 also underwent the phase transition of the semiconductor–semiconductor type (T_c ~ 155°C (*2*)).

Figure 1 represents VLα-spectra of the compounds under investigation. The spectrum of an oxide V_2O_3 differs from that of pure metal by a subband *B*. At further increases of the oxygen content in an oxide a redistribution of intensity and an Lα-spectrum takes place: The intensity of the subband *B* increases while that of the subband *A* decreases.

The calculations of VO, V_2O_3, VO_2, and V_2O_5 were carried out by the Muliken–Wolfsberg–Helmholz method in the cluster approximation (*10*). They showed that the subband *B* is to be related to the oxygen 2*p*-states hybridized with V3*d*-states and that the subband *A* is predominantly due to V*3*d states. The increase of subband *B* intensity can be taken thus to indicate an increased population of the corresponding molecular orbitals by atomic 3*d*-orbitals. In other words, the sequence of oxides under examination exhibits O2*p*–V*3*d interaction. Besides, a long-wave structure *C* and *D* caused by the O2*s*–V3*d*4*s* hybridization arises in the spectra of oxides. Also a displacement of the whole Lα-spectrum to high energies occurs at an increase of the oxygen content (see Table I).

We can conclude from an electroneutrality condition that the oxides V_3O_5, V_4O_7, and V_6O_{11} contain ions V^{3+} and V^{4+} in proportions 2 : 1, 1 : 1, and 1 : 2, respectively. To check this conclusion we have added up graphically the

TABLE I

THE CHARACTERISTICS OF THE Lα-EMISSION BANDS OF VANADIUM IN A PURE METAL AND IN ITS OXIDES

Compound	Subband shifts (eV) *A*	*B*	Lα-band width Experimen.	Additive
V	—	—	3.8	—
V_2O_3	+1.4	−4.9	10.5	—
V_3O_5	+2.1	−3.9	10.9	10.9
V_4O_7	+1.9	−4.5	11.0	11.0
V_6O_{11}	+1.4	−3.6	11.5	11.2
VO_2	+2.0	−2.7	11.6	—
V_6O_{13}	+2.9	−2.0	9.7	11.3
V_3O_7	+2.5	−2.7	10.0	10.6
V_2O_5	+3.4	−0.9	9.2	—
Error	±0.5	±0.5	±0.2	

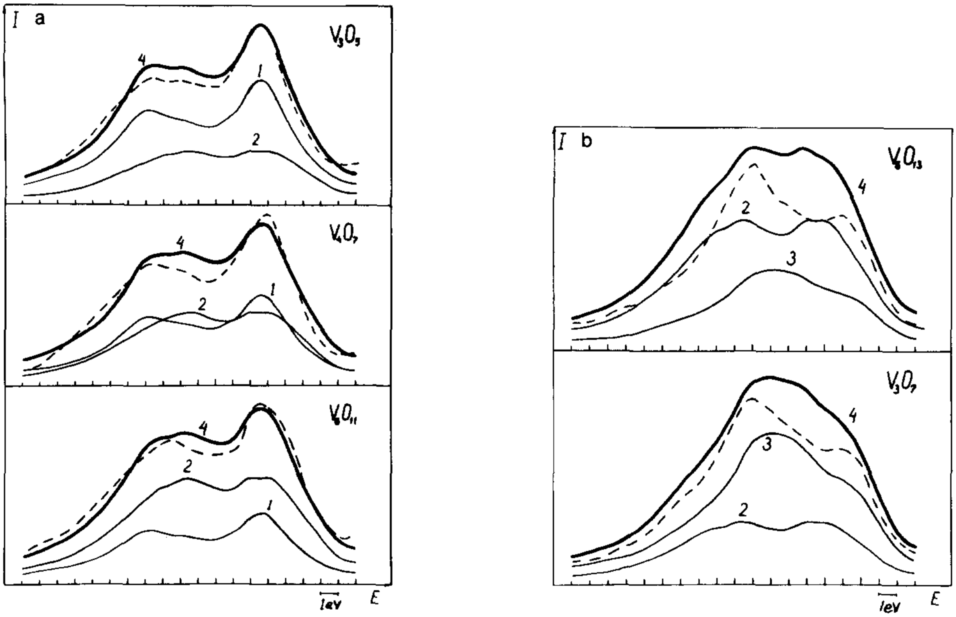

FIG. 2. A comparison of experimental and additive VLα-spectra; (a) in V_3O_5, V_4O_7, V_6O_{11} oxides; (b) in V_6O_{13} and V_3O_7 oxides; 1, a spectrum of V_2O_3, 2, VO_2, 3, V_2O_3, 4, additive spectra; dashed curve, the experimental spectra.

spectra of V_2O_3 and VO_2 in proportions given above (which were taken from the integral intensities of the VLα-spectra of V_2O_3 and VO_2). Thus the obtained additive spectra of the three intermediate oxides, are represented in Fig. 2a. It is seen that the form of the obtained spectra is the same as that of the experimental ones. The experimental and additive band widths measured at a half-maximum of intensity, show good agreement as well (see Table I). Differences are observed only in the relative intensities of *A* and *B* subbands.

Consequently we may consider the oxidation states of vanadium ions in the Magneli phases to be close to those of V_2O_3 and VO_2. The lifetime of inner level hole ($\sim 10^{-15}$sec (*11, 12*)) is thus long enough for the two oxidation states of vanadium ions not to be averaged. These coexisting oxidation states are V^{3+} and V^{4+}, and the frequency of charge fluctuations must not exceed 10^{-15} sec. The NMR investigations of the Magneli phases (*13, 14*) give $\nu_{\text{fluc}} \geqslant 3.10^7$ sec^{-1}. So we have for the charge fluctuations frequency: 10^{15} sec^{-1} $> \nu_{\text{fluc}} \geqslant 3.10^7$ sec^{-1}.

By comparing experimental and additive spectra we neglect the differences in crystallochemical characteristics for vanadium ions as existing in the Magneli-type phases and V_2O_3 and VO_2 oxides. The comparison was based, first, on the crystal structure of Magneli oxides built up from alternate layers of the rutile and corundum types (*15*) and second, on the octahedral coordination of vanadium as in Magneli phases as in V_2O_3 and VO_2. The fact that under the room temperature the mean V–O distances of four unequivalent V-positions in V_4O_7 do not greatly vary and have values intermediate between the values of V–O distance in V_2O_3 and VO_2 (*16, 17*) do not contradict conclusions made in the present study, since the individual atoms may not follow such rapid charge fluctuations and will react to the averaged charge distribution.

The same procedure of superposition was applied to V_6O_{13} and V_3O_7 oxides. The spectra of VO_2 and V_2O_5 were taken in proportions

2:1 for V_6O_{13} and 1:2 for V_3O_7. As is seen from Fig. 2b the form of additive spectra differs from that of experimental ones. Besides, the widths of additive spectra of these oxides are greater than the widths of experimental spectra (see Table I).

The result indicates that the oxidation states of crystallographically nonequivalent vanadium atoms do not differ to a great extent. That is, the lifetime of the inner level hole is sufficient for the oxidation states to reach an averaged value, so that for the frequency charge fluctuations in the oxides V_6O_{13} and V_3O_7 the condition must be fulfilled $\nu_{\text{fluc}} > 10^{15}\ \text{sec}^{-1}$.

Such rapid charge fluctuations can be caused by strong cation–anion–cation interaction. Direct cation–cation interaction seems to be rather weak, since the smallest V–V distance in these oxides (3.009 Å) exceeds the critical V–V distance (2.94 Å) (*18*) necessary for the band formation. According to Goodenough (*19, 20*) a partly filled π antibonding band can arise through the overlap by way of oxygen ions.

In the case of V_6O_{13} and V_3O_7 spectra the differences in the crystal structures of V_6O_{13}, V_3O_7, V_2O_5, and VO_2 oxides were not taken into account either. For V_3O_7 the result appears the most unexpected as there are five crystallographically nonequivalent sites for vanadium ions in the crystal lattice. Two of these sites are octahedrally coordinated, and three others, fivefold coordinated, the mean V–O distances closely following the mean V–O distance in VO_2 and V_2O_5 (*9*). One could expect, thus, a coexistence of V^{4+} and V^{5+} ionic states.

It may be noted that all conclusions we have reached in this work are in a full agreement with those obtained in the course of investigations of $VK\beta''\beta_5$-spectra from these oxides (*6*).

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