A Mössbauer study of pentavalent iron in a vanadium(V) oxide matrix

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The formation of iron in the 5+ oxidation state was observed in iron-doped vanadium(V) oxide; this state is characterised by a singlet with the isomer shift $\delta = -0.56\pm0.01$ mm s^{-1} relative to α-iron in the Mössbauer spectrum at room temperature.

The preparation and study of the elements in unusual oxidation states are an important branch of present-day inorganic chemistry. These species are of considerable interest because, on the one hand, they are of practical importance creating compounds and materials with new and unusual properties. On the other hand, the data on the physico-chemical properties of these systems expand the experimental basis of empirical laws that remain still quantitatively unsubstantiated.

In this context, a study of iron in high oxidation states is of paramount importance. Indeed, the wine-coloured FeO_4^{2-} ion has been known since the 19th century. However, the compounds of iron in the oxidation states higher than 4+ are known as only a few of examples to the present day, and the data on their chemical properties are limited.

The compounds of iron in high oxidation states are of particular interest in Mössbauer spectroscopy. Iron seems to be the most convenient element for Mössbauer studies. The correlation between the Mössbauer spectral characteristics and the oxidation state of iron allows us to reveal the potentialities of this technique for studying the electronic and geometric structures of substances.

A study of various compounds doped by different elements is used in modern chemistry and related sciences for determining the positions and properties of dopants. In particular, both simple and sophisticated oxides doped by iron have long been examined by Mössbauer spectroscopy.[1] This approach is promising for the preparation of derivatives of the element in uncommon oxidation states.[2]

We decided on a vanadium(V) oxide matrix for stabilising iron in the unusual 5+ oxidation state for the reasons given below. First, the ionic radii of vanadium are close to the radii of isovalent iron ions.[3–7] Thus, it is reasonable in terms of crystallography to expect the formation of the Fe^{5+} ion by isovalent isomorphous substitution of iron for vanadium in V_2O_5. Second, V_2O_5 is the highest oxide of vanadium. Consequently, it cannot be a reducing agent for the highly oxidised iron ions. Finally, V_2O_5 melts at a moderate temperature (674 °C) and remains stable even above the melting point.[8] Thus, the problem of uniform iron distribution in the bulk of V_2O_5 can be solved, for example, by dissolving Fe_2O_3 in a V_2O_5 melt.

Here we report the data on the 5+ oxidation state of iron in a vanadium(V) oxide matrix.

Iron was introduced into V_2O_5 by dissolving $^{57}Fe_2O_3$ in molten vanadium(V) oxide in a platinum crucible at about 700 °C in an oxygen atmosphere. Next, the melt was cooled rapidly by immersing the crucible in metallic mercury. The iron content of the product was approximately 1 mol% on a vanadium basis.

Absorption Mössbauer spectra were measured on a Perseus spectrometer (a modified instrument from the Research Institute of Instrument-making, Moscow)[9] operating in a constant velocity regime; the control and correction (stabilisation) of the spectrometer vibrator velocity were performed with a laser interferometer. Standard γ-radiation sources of ^{57}Co in chromium metal matrices with the activities up to 35 mCi (Cyclotron Co., Ltd., Obninsk, Russia) were used. Isomer shifts are given with respect to α-iron.[10] The Mössbauer nomenclature is given according to the recommendations submitted to IUPAC by Intrnetional Board on the Application of the Mössbauer Effect (IBAME).[11] X-ray measurements were carried out on a DRON-3M diffractometer (Russia) using CuKα radiation and a Ni filter.

Hardening of the iron-doped vanadium(V) oxide melt leads to the formation of a black glassy product, which becomes dark brown in a fine powder.

An X-ray powder diffraction study of this product revealed no phases other than V_2O_5. The X-ray diffraction patterns are similar to those of pure V_2O_5 (both hardened under the above conditions and non-hardened) and correlate with the published data.[12]

Figure 1(*a*) shows a typical room-temperature Mössbauer spectrum of the substance. To a first approximation, the spectrum contains two resolved lines with different intensities and widths on the background of extended absorption. The spectrum can be formally described by a model containing three components, a singlet, a doublet and an unresolved constituent of extended absorption.

The envelope of the extended absorption can be formally described, *e.g.*, by a broad singlet.† However, it is evident that this component results from magnetic interactions in the substance, as confirmed by low-temperature measurements.

Indeed, the lines of the hyperfine magnetic structure are resolved in the spectrum [Figure 1(*b*)] as the temperature is decreased up to –196 °C. However, the resolution is inadequate, and it is most likely that the lines are related to two sextets. Moreover, the central portion of the spectrum becomes more complicated. Thus, it is impossible to suggest an unambiguous model for the description of the spectrum. However, an analysis of the spectrum shows that the presence of a divalent iron derivative among magnetic species is quite possible.

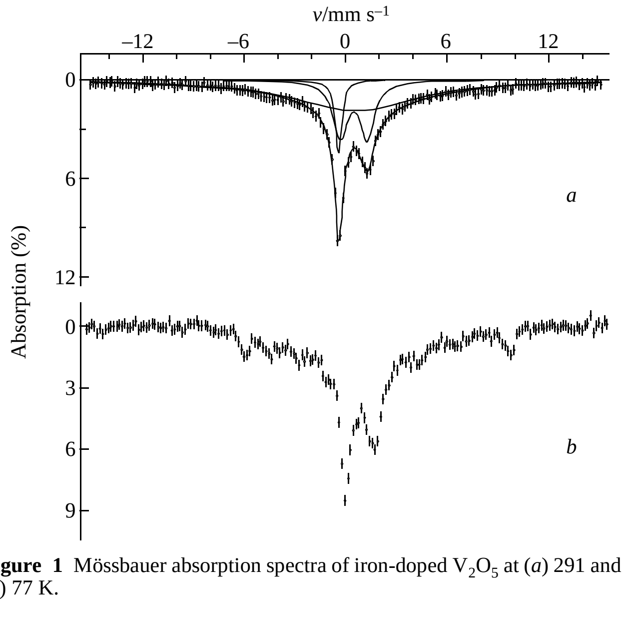

Figure 1 Mössbauer absorption spectra of iron-doped V_2O_5 at (*a*) 291 and (*b*) 77 K.

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† In the spectrum, the parameters of this line are $\delta = 0.45\pm0.06$ mm s^{-1} and $\Gamma_{exp} = 8.8\pm0.6$ mm s^{-1}.

An increase in the sample temperature up to 400 °C allowed us to exclude the presence of unresolved magnetic structures in the spectrum, and the shape of the central portion of the spectrum remained unchanged. However, the spectrum changed at this temperature because of the annealing of the substance.

It is safe to say that the right component of the central portion of the spectrum [Figure 1(*a*)] is due to a trivalent iron doublet. The fact that the doublet line widths are considerable[‡] suggests the presence of several different trivalent iron species, which are similar in nature and geometrical arrangement. Indeed, the doublet parameters, especially the quadrupole splitting and line widths, changed with a little variation of the synthesis conditions and the iron content of the system. This part of the spectrum can correspond to trivalent iron ions occupying vacancies that are available in the vanadium(V) oxide structure[13] and can also be formed under deformation of the V_2O_5 crystal lattice in the course of doping of this oxide by iron.[14] Of course, an attempt to describe the substance on the basis of the vanadium(V) oxide crystal structure is provisional, because the substance can contain an amorphous phase in considerable amounts.[15]

The singlet with the parameters $\delta = -0.56\pm0.01$ mm s^{-1} and $\Gamma_{\text{exp}} = 0.41\pm0.02$ mm s^{-1} is of primary interest [Figure 1(*a*)]. The relationship between the isomer shift and the oxidation state of iron in an oxygen environment is well known.[16] Isomer shifts for hexavalent iron derivatives were measured in a study of alkali and alkaline earth metal ferrates, in which the Fe^{6+} ion is in the tetrahedral arrangement of oxygen ions. The room-temperature isomer shift values for these compounds are in the range from -0.98 to -0.88 mm s^{-1}.[16,17] In addition, the isomer shift of sodium ferrate(VI) was found to be equal to -0.80 mm s^{-1} at room temperature.[18] The isomer shift for pentavalent iron is known only for the compound La_2LiFeO_6 with the octahedral coordination of the Fe^{5+} ion, and it is equal to -0.41 mm s^{-1}.[5,6] According to the well-known fact that the isomer shift of iron decreases with decreasing coordination number,[16,19] we can conclude that the isomer shift $\delta = -0.56$ mm s^{-1} corresponds to the 5+ oxidation state of iron with a coordination number lower than six.

The position of the line with $\delta = -0.56$ mm s^{-1} remained unchanged with varying the synthesis conditions and the iron content. A change in the temperature of measuring the spectrum leads to a systematic drift of the line; this drift is characterised by the value of $d\delta/dT = (5.0\pm0.2)\times10^{-4}$ mm s^{-1} K^{-1} in the temperature range examined. The fact that noticeable changes in the shape of the spectrum lines in the central portion, namely, the ratios of intensities and widths, were not observed in the temperature range from -196 to 400 °C did not allow us to consider the asymmetry of the central portion of the spectrum as a result of the Gol'danskii–Karyagin effect[20] or the Blume mechanism.[21] Because of this, the suggested interpretation of the asymmetry observed as a result of the appearance of the singlet with $\delta = -0.56$ mm s^{-1} seems to be reasonable.

The possible existence of divalent iron in the substance is not surprising; moreover, in our opinion, this fact can be an additional argument in support of the formation of iron in a higher oxidation state. In fact, the presence of divalent iron can correspond either to the reduction of Fe^{3+} placed in a V_2O_5 matrix to Fe^{2+} and the release of oxygen or to the disproportionation of trivalent iron $3Fe^{3+} \rightarrow Fe^{5+} + 2Fe^{2+}$, which was initially introduced into the system as Fe_2O_3. As mentioned above, vanadium(V) oxide cannot be a reducing agent. However, note that the reduction of trivalent iron to a divalent state was not detected under similar experimental conditions.[14,15]

If the system is considered on a basis of the crystal structure of vanadium(V) oxide, we can suggest that the formation of pentavalent iron takes place by isovalent isomorphous replacement of vanadium with iron in the V_2O_5 structure. The coordination polyhedron of vanadium in V_2O_5 can be considered as a strongly distorted octahedron.[22] This distortion is significant, so that the coordination polyhedron is, in fact, an irregular trigonal bipyramid,[14,22] which corresponds to the coordination number 5. Further distortion, which appears with the introduction of iron into the system as a result of the difference in the ionic radii of vanadium and iron and of the filling of vacancies in the vanadium oxide structure by Fe^{2+} and Fe^{3+} ions, can lead to a decrease in the coordination number.[14]

Thus, we found for the first time that pentavalent iron can be formed in the course of doping vanadium(V) oxide by iron.

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[‡] The parameters of this symmetric doublet in the spectrum are $\delta = 0.34\pm0.01$ mm s^{-1}, $\Delta = 0.34\pm0.01$ mm s^{-1} and $\Gamma_{\text{exp}} = 1.02\pm0.04$ mm s^{-1}.