A Study of the Paramagnetic Center in Vanadium Pentoxide

Kozo HIROTA, Keiji KUWATA and Yoshiya KERA

Faculty of Science, Osaka University, Toyonaka, Osaka

(Received March 23, 1970)

ESR studies of the V(IV)ion in vanadium pentoxide have been extensively carried out. The use of a single crystal gives more detailed information regarding the structure of the paramagnetic centers in V_2O_5.[1] In the present paper the esr spectrum of a new center in V_2O_5 is shown, and the mechanism of its formation is discussed.

The single crystal was prepared by the zone-melting method from pure V_2O_5 powder. The *g*-factor and the hyperfine coupling constant were determined at 77°K with DPPH ($g=2.0035$) and the Mn(II) ion in magnesium oxide, respectively.

When the static magnetic field was applied in parallel with the *b*-axis, clear hfs of 27 lines appeared, as is shown in Fig. 1; as the direction of

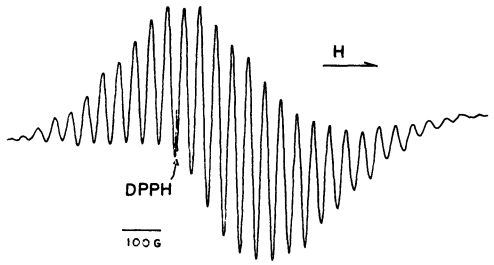

Fig. 1. ESR spectrum of a V_2O_5 single crystal with the static field applied in parallel with the crystallographic *b*-axis.

the field deviated from the *b*-axis on both the *ba*- and *bc*-planes, the hf splitting quickly decreased. On the basis of this finding, one of the principal axes for the hf interaction was estimated to be nearly the *b*-axis, and the maximal principal value was estimated to be 43.3 gauss.

The number of lines in hfs and the polynominal distribution of their intensities indicate the existence of a magnetic center in which four ^{51}V nuclei ($I=7/2$) interact equally with an unpaired electron.

The magnetic center including four ^{51}V atoms has been briefly discussed by Ioffe and Patrina,[1c] but neither detailed experimental results nor discussion was given regarding its structure.

The principal components of the *g*-tensor for this center were $g_{xx}=1.974_9$, $g_{yy}=1.988_7$, and $g_{zz}=1.931_3$, and the *x*, *y*, and *z*-axes nearly accorded with the *a*, *c*, and *b*-axes of the crystal with an orthorhombic symmetry, respectively. The relationship among the components of the *g*-tensor indicates that the V(IV) ion is in the field of fourfold symmetry.[2]

The fourfold symmetry can be obtained when an oxygen ion on the *b*-axis is lost. A pair of V ions formed by the elimination of such an oxygen ion had been proposed by Gillis *et al.*[1] as the paramagnetic center in V_2O_5.

On the basis of the present study, two neighbouring pairs of V ions were assumed to constitute a paramagnetic center containing four V atoms. The removal of the I and II oxygen ions in Fig. 2 produces such pairs (1-2 and 3-4 in Fig. 2). Similarly, 1-2 and 1′-2′ pairs, or 3-4

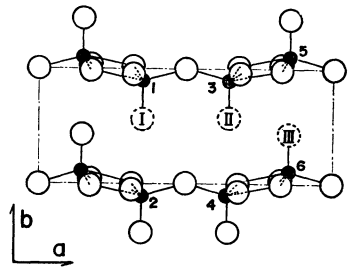

Fig. 2. Arrangements of paramagnetic center in the V_2O_5 crystal, whose structure was taken from Ref. 3. (large circles denote oxygen ions; small circles denote vanadium ions. For example, V atoms of 1′ and 2′ are placed just behind the 1 and 2 V atoms, respectively.)

and 5-6 pairs, can equally form the center. An unpaired electron is assumed to interact equally with the four V ions through fast exchange between these pairs. The center of this kind, as in Eq. (1), can be formed either by the direct elimination of two neibouring oxygen ions, or by the migration of the oxygen vacancy through the crystal lattice to form the two pairs of V ions:

$$2(V^{5+}-O^{2-}-V^{5+}) \rightarrow \begin{matrix} V^{5+}\ldots V^{5+} \\ \vdots \quad\quad \vdots \\ V^{5+}\ldots V^{4+} \end{matrix} + 2O + 3e^- \quad (1)$$

It is worthy of mention that the formation of such a defect could be predicted from the study of catalytic activity of this oxide.[4]

1) a) J. L. Ragle, *J. Chem. Phys.*, **38**, 2020 (1963); b) E. Gillis and E. Boseman, *Phys. Stat. Sol.*, **14**, 337 (1966); c) V. A. Ioffe and I. B. Patrina, *Sov. Phys.-Solid State*, **10**, 639 (1968).

2) H. G. Hecht and T. S. Johnston, *J. Chem. Phys.*, **46**. 23 (1967).

3) A. Byström, K. A. Wilhelmi and O. Brotzen, *Acta Chem. Scand.*, **4**, 1119 (1950).

4) K. Hirota, Y. Kera and S. Teratani, *J. Phys. Chem.* **72**, 3133 (1968).