Electron spin resonance of some vanadium oxides

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Vanadium oxides, except V₂O₅, show phase transitions at critical temperatures (T₁). Above T₁ they show metallic behaviour and are semiconductors below T₁. Electron spin resonance spectrum of these oxides were recorded at 298 K and 120 K. The ESR signal is obtained only when the compound is in the semiconducting state. It is assumed that the signal is caused by V⁴⁺ ions.

Vanadium oxides show interesting solid state properties. They undergo semiconductor-to-metal transition at their phase transition temperature (T₁) except V₂O₅ and have the potential to be exploited as solid state devices such as thermistors, current limiters, precision thermometers, etc. These oxides are semiconducting below T₁ and show metal-like behaviour above T₁. They show an abrupt jump in electrical resistivity by a large factor at T₁. This rapid change in electrical resistivity over a narrow temperature range is an important attribute of good thermistor materials.

Electrical, magnetic, structural and thermal studies of these oxides have been reported elsewhere. These oxides undergo phase transitions at different critical temperatures mainly due to crystallographic transformation. This note deals with electron spin resonance spectra of these compounds recorded at room temperature and at 120 K.

Vanadium pentoxide is prepared by thermal decomposition of ammonium meta vanadate at 823 K over 6 h. The V₂O₅ thus obtained was reduced to V₂O₃ with purified hydrogen gas flow at 1073 K over 7 h. Other oxides such as VO₂, V₃O₇, V₄O₉ and V₅O₉ were prepared by heating an appropriate mixture of V₂O₅ and V₂O₃ in an evacuated (~1.3 x 10⁻³ pa) quartz ampoule; the detailed preparative methods are reported elsewhere. The polycrystalline materials thus prepared were characterized by X-ray diffractograms recorded on a Philips X-ray diffractometer (PW 1140) using Cu-Kα radiation filtered through a nickel absorber.

The ESR spectra were taken at the x-band on a Varian E-112 spectrometer at 298 ±1 K and 120 ±2 K. The sample was mounted in a quartz tube and TCNE was used as a field calibrant taking its g-value as 2.00277.

For each of the vanadium oxide compounds, absorption lines were observed with g varying from 1.972 to 1.952 at room temperature except in the cases of V₂O₃, V₃O₇ and V₅O₉. For the compounds which did not show an ESR signal at room temperature the spectra were recorded at temperatures below their transition temperatures (T₁) and signals were observed with g between 1.954 and 1.943 as shown in Table 1. For example, V₂O₅, V₃O₇ and V₅O₉ show metal-like behaviour at room temperature and did not show an ESR signal, but when the temperature was maintained at 120 ±2 K they showed ESR signals. VO₂ and V₂O₃ are semiconductors at room temperature and showed an ESR signal. They have T₁ at 341 K and 424 K respectively and above T₁ they did not show any ESR signal. V₂O₅, when tried at 150 K for ESR resonance did not show any signal but at 120 K showed a signal. V₃O₇ has T₁ at 129 K. It may be concluded that when these oxides are in a metal-like state they do not show an ESR signal; on the contrary when the same compounds are in a semiconducting state they become ESR active. When the compound is in the metallic state the ESR is not always detectable because the line width is determined by the spin-lattice relaxation time, which decreases as spin-orbit coupling coefficient increases. The signal from these metals may be so broad that it is unobservable. Since vanadium has 7/2 nuclear spin, it is expected to show hyperfine structure, but it is not observed. This is because the vanadium oxides contain more concentration of V⁴⁺ ions which give a single signal due to dipolar broadening destroying the hyperfine structure. If V₂O₅ is diluted (1-2%) in an inert matrix like silica, the hyperfine structure may be observed as in the cases of vanadium complexes.

From Table 1, it is seen that the g-factor increases monotonically with an increase of the oxygen to vanadium ratio in the compounds, and the line width observed is in the range 100-310.
Table 1 — ESR data of vanadium oxides

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$T_c$ (°K)</th>
<th>g-factor (298 ± 1K)</th>
<th>g-factor (120 ± 2K)</th>
<th>Peak to peak line width (gauss)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V$_2$O$_7$</td>
<td>170</td>
<td>No signal</td>
<td>1.943</td>
<td>320</td>
</tr>
<tr>
<td>V$_2$O$_5$</td>
<td>424</td>
<td>1.952</td>
<td>—</td>
<td>170</td>
</tr>
<tr>
<td>V$_3$O$_7$</td>
<td>239</td>
<td>No signal</td>
<td>1.953</td>
<td>360</td>
</tr>
<tr>
<td>V$_4$O$_9$</td>
<td>129</td>
<td>No signal</td>
<td>1.955</td>
<td>330</td>
</tr>
<tr>
<td>VO$_2$</td>
<td>341</td>
<td>1.955</td>
<td>—</td>
<td>140</td>
</tr>
<tr>
<td>V$_2$O$_3$</td>
<td>Nil</td>
<td>1.972</td>
<td>1.963</td>
<td>100</td>
</tr>
</tbody>
</table>

gauss. Belyakov et al$^9$ concluded that V$^{3+}$ ions could not be responsible for the resonance absorption. It is assumed that in vanadium oxides there is a corresponding concentration of V$^{4+}$ ions, which increases as oxygen content increases.

The V-O system in hydrogen reduction and heating in vacuum can produce oxygen vacancy centres. Since oxygen vacancy dominates in these compounds, the different types of defect centres are likely to influence ESR absorption and in the semiconducting state they may be ESR active.

Marezio et al$^6$ showed in their refinement of the crystal structure of V$_2$O$_7$ that the metallic phase was characterized by an almost complete disorder of V$^{3+}$ and V$^{4+}$ cations. Below $T_c$ these cations get ordered so that the 3113 chains become richer in V$^{4+}$ and the 4224 chains, richer in V$^{3+}$. Crystallographic studies carried by Marezio et al$^7$ have claimed that all the V$^{3+}$ sites and half of the V$^{4+}$ sites in the semiconducting state undergo structural pairing. Metal-to-semiconductor transitions are attributed to a crystallographic distortion by which the localization of electron at specific V-sites is made favourable. Such distortion removes the degeneracy of the $t_{2g}$ orbital triplet leading to an increased spin lattice relaxation time which decreases the line-width, giving rise to an ESR signal.

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References