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d-Electrons in Crystalline and Amorphous V_2O_5 and MoO_3 Compounds*

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The characteristic features of electron spin resonance (ESR) spectra of nonstoichiometric V_2O_5 and MoO_3 are surveyed.

In their stoichiometric form V_2O_5 and MoO_3 should be diamagnetic insulators. The 3*d* and 4*d* orbitals are not occupied (d^0 configuration). Various possibilities, however, are known to produce nonstoichiometric compounds of V_2O_5 and MoO_3 which contain a nonintegral number of *d* electrons per transition element lattice site: formation of transition element bronzes (*1*), substitution of transition element ions, oxygen deficiency, and adding of glassformers, etc.

The behavior of these additional *d* electrons is essentially determined by electron–phonon interaction which favors polaron formation, by interaction with nonperiodic Coulomb fields which may lead to Anderson localization, by electron correlation energy, etc. (*2*).

Electron spin resonance (EPR) is a powerful tool used to investigate localized *d* states and thus to gain information on the electronic structure of these compounds.

Because of spin $S = 1/2$ we expect one electronic transition in the ESR spectra of *d* electrons on nonstoichiometric V_2O_5 and MoO_3 compounds. The *g*-tensor, which is derived from the resonance fields, yields information on the ground state and the crystal field splitting. From the hyperfine interaction of the *d* electrons with vanadium ($I = 7/2$) or molybdenum nuclei ($I = 5/2$) we may deduce the extent of localization or delocalization of the *d* states. From linewidth studies we learn about relaxation times, mobile behavior, etc.

ESR investigations of different classes of nonstoichiometric V_2O_5 and MoO_3 compounds are known (*3*, *4*). This paper surveys the characteristic features of the ESR signals of some of these compounds, where the measurements were performed over large

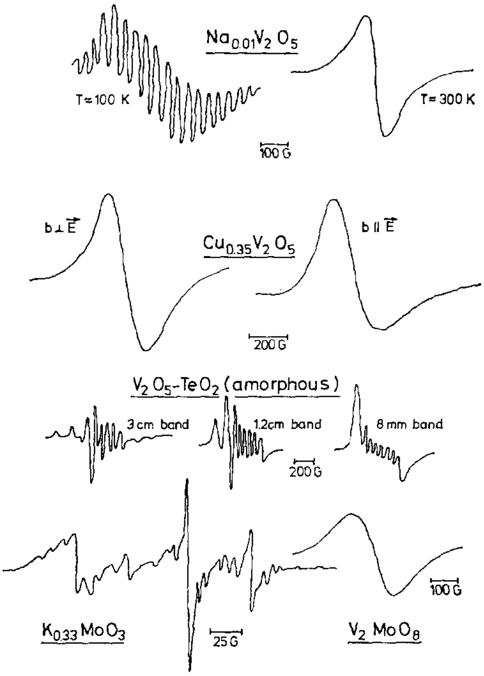

FIG. 1. Review of ESR spectra of some nonstoichiometric V_2O_5 and MoO_3 compounds.

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TABLE I

FEATURES TYPICAL OF THE ESR SPECTRA OF SOME NONSTOICHIOMETRIC V_2O_5 AND MoO_3 COMPOUNDS, AND THEIR INTERPRETATION

Compound	Essential features of the ESR spectra	Interpretation
$Na_{0.01}V_2O_5$ $T \approx 4°K$	Inhomogeneously broadened gaussian line	Na^+ in an asymmetric position in respect to the neighbored vanadium sites
$T \approx 100°K$	Resolved *HF*-splitting, equal interaction with four vanadium nuclei	Anderson localization of $3d$ electrons on four vanadium sites within the nonperiodic Coulomb field of the Na^+ ion, distances between Na^+ ion and four vanadium sites are equal (symmetric position)
$T \approx 300$	Narrowed lorentzian line	Hopping mechanism of d electrons causes a line narrowing, hopping frequency is larger than hyperfine splitting in frequency units
$Cu_xV_2O_5$ $0.26 < x < 0.64$	g shift negative; asymmetry of the structureless ESR line depends on orientation of the crystal with respect to the E-field of the microwave	Incorporation of copper as Cu^+ ion; strong anisotropy in the electrical conductivity; one-dimensional metallic conductivity along monoclinic b-axis
$K_{0.33}MoO_3$ $T \sim 40°K$	Resolved *HF*-splitting, relatively small linewidth, low signal intensity	Most of the $4d$ electrons are spin-paired ($S = 0$); deviation of x from the ideal value of $x = 1/3$; delocalization of $4d$ electrons over different number of Mo orbitals
MoO_3–TeO_2 V_2O_5–TeO_2 Amorph.	Resolved *HF*-splitting, the linewidth increases with resonance frequency	Localization of d electrons on one vanadium or molybdenum site; well defined microenvironment; hopping frequency even at room temperature smaller than hyperfine splitting in frequency units
$V_2MoO_8 =$ $V_2O_5 \cdot MoO_3$	Extremely narrowed linewidth, orientation dependence typical for narrowing of a large hyperfine splitting	Localization of the d electrons on vanadium $3d$ sites but not in molybdenum $4d$ orbitals; hopping mobility of the d electrons

temperature regions, and at different resonance frequencies.

Figure 1 shows typical ESR spectra of d electrons in the mentioned compounds. In some cases a *HF* splitting is resolved, in other compounds a structureless signal occurs, the spectra change with temperature and (in the amorphous compounds) with frequency. The negative g-shift compared with the value of free electrons (g-factors around 1.96) shows in a unique way that the ESR signals are caused by d electrons in a noncubic environment.

Table I summarizes the essential features of the ESR spectra and the corresponding interpretation.

References

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