

Electronic properties of the $M_2InV_3O_{11}$ (M(II)=Zn(II) and Co(II)) compounds



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Abstract

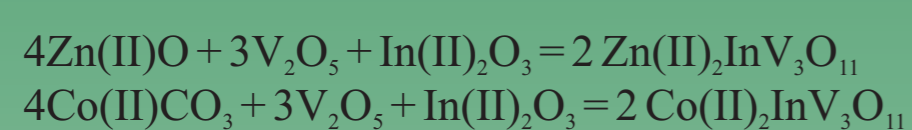
The electronic properties of the multicomponent vanadate oxide (M(II)=Zn(II) and Co(II)) have been investigated by electrical conductivity and electron paramagnetic resonance (EPR) measurements. Both compounds exhibit semiconducting behavior. Replacement of the non-magnetic Zn(II) cations with magnetic Co(II) ions results in a significant drop of the electrical conductivity and an increase of the activation energy. The activation energies were determined to be $E_a=0.43(3)$ eV at $T<180$ K and $E_a=0.18$ eV at $T>200$ K for $Zn_2InV_3O_{11}$, in contrast to the value of $E_a=0.35$ eV derived at high temperatures for $Co_2InV_3O_{11}$. EPR spectroscopy shows the presence of VO^{2+} vanadyl ions for both compounds, while the presence of divalent cobalt ions is identified at low temperatures for the $Co_2InV_3O_{11}$ oxide. The concentration of the VO^{2+} vanadyl ions is about one order higher for the sample without magnetic ions. It is suggested that the increased concentration of VO^{2+} ions could be responsible for the enhanced conductivity of $Zn_2InV_3O_{11}$.

Introduction

Indium oxide is one of the most important compounds for applications in optoelectronic technology [1,2] because of its high electrical conductivity [3]. Both structural defects caused by oxygen deficiency and intentional doping play a very important role in the transport properties of these oxides. Other compounds containing indium exhibit very interesting electronic properties, e.g. InN that was found to be an n -type semiconductor with electron concentrations in the range of 10^{17} – 10^{21} cm^{-3} and a small band gap value of about 0.7 eV [4–6]. Recently, some new multicomponent vanadate oxide indium materials with vanadium ions have been prepared and investigated by electron paramagnetic resonance (EPR), where vanadium ions at the lower oxidation state have been identified [7]. Moreover, mixed vanadate oxides are very interesting for their catalytic properties, especially ortho- and divanadate (V) compounds [8]. The aim of this work is the preparation of the new mixed indium-vanadium oxides $M_2InV_3O_{11}$, M(II)=Zn(II) and Co(II) with magnetic (Co) and non-magnetic (Zn) ions in the cation position and the study of concomitant variations in their electronic properties by means of EPR spectroscopy and dc resistivity measurements.

Experimental

Polycrystalline samples of $M_2InV_3O_{11}$, M(II)=Zn(II) and Co(II) were prepared by using the solid state reaction method [9,10]:



The samples $Zn_2InV_3O_{11}$ and $Co_2InV_3O_{11}$ are yellow and black, respectively and have been found to crystallize in the triclinic system [11].

The EPR spectra were recorded using a standard X-band spectrometer type Bruker E500 ($\nu=9.455$ GHz) with magnetic field modulation of 100kHz. The magnetic field was scaled with a NMR magnetometer. The samples, containing 30 mg of the substance in the form of fine powder, without any cement-dielectric, were sealed into 4 mm in diameter quartz tubes. The measurements were performed in the temperature range of 4 to 290 K using an Oxford nitrogen flow cryostat and a standard hot air flow system.

DC electrical resistivity measurements were performed in the temperature range of 90–320 K for small pellets (about 6 mm in diameter, with a thickness of 3–4 mm) prepared under pressure of 70–80 bar using a special dielectric glue. The resistance was measured with a Keithley 181 electrometer according to the two-point geometry, with highest limit that of 2×10^{11} Ω for the circuitry of the experiment.

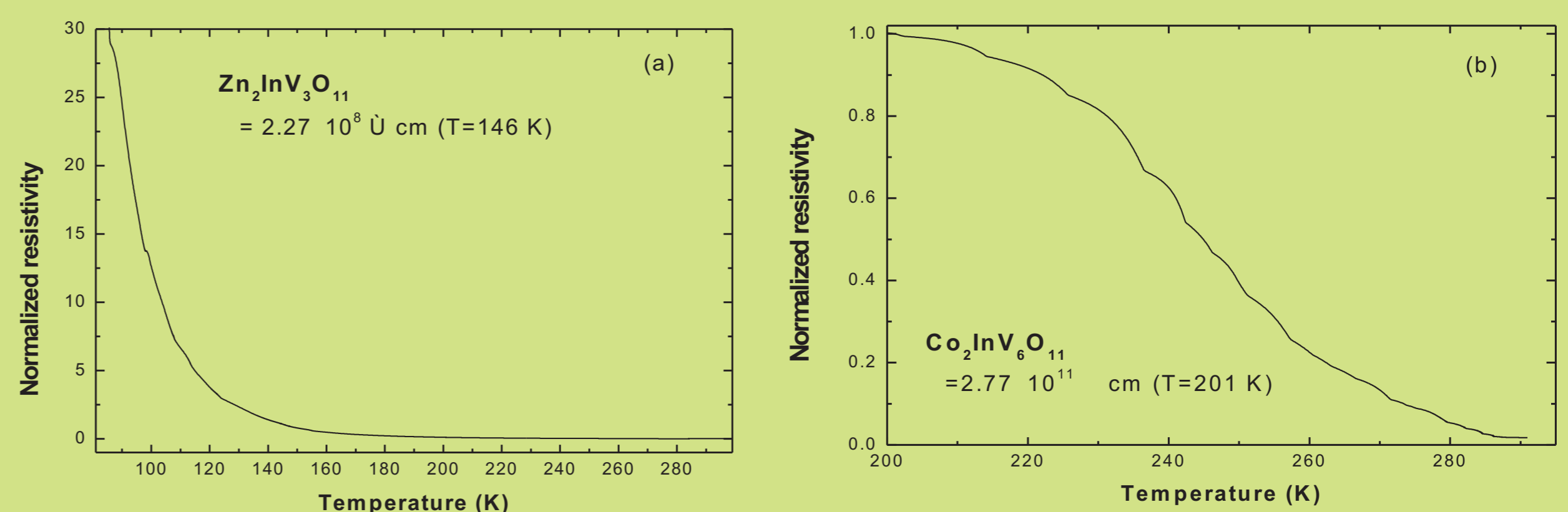


Figure 2 Temperature dependence of the normalized resistivity for the vanadate oxides, (a) $Zn_2InV_3O_{11}$ and (b) $Co_2InV_3O_{11}$.

Experimental results

Figure 1 compares the EPR spectra of the multicomponent vanadates $Co_2InV_3O_{11}$ and $Zn_2InV_3O_{11}$. For the latter compound, detailed EPR measurements as a function of temperature have been recently reported [7]. The EPR spectra of $Co_2InV_3O_{11}$ revealed an additional resonance line arising from high spin Co^{2+} ions in orthorhombic crystal field symmetry [12,13]. The concentration of vanadium ions at the lower oxidation decreased significantly (about one order of magnitude), especially the VO^{2+} vanadyl ions for the sample with magnetic ions (Fig. 1).

The temperature dependence of the EPR spectra of $Zn_2InV_3O_{11}$ and $Mg_2InV_3O_{11}$ have shown the presence of a complex of vanadium ions with lower valence, while resonance lines at lower magnetic field have been attributed to three valence indium ions [7,14]. A recent study of the temperature dependence of the EPR spectra of $Zn_2InV_3O_{11}$ has revealed the presence of monomeric and dimeric vanadium complexes. The EPR spectra were described by the hyperfine interaction of VO^{2+} centers in axial symmetry. The latter component consists of two sets of eight partially overlapping lines and it is due to the interaction of the 3d electron spins ($S=1/2$) with the ^{51}V nuclei ($I=7/2$, abundance 99.75%). These lines can be described by an axial spin-Hamiltonian of the form: $H=\mu_B[g_1B_S+g_2(B_S)_z+A_1S_zI_z+A_2(S_zI_z+S_xI_x+S_yI_y)]$ with parameters: $g_1=1.93$, $g_2=1.94$ and $A_1=180 \times 10^4$ cm^{-1} , $A_2=50 \times 10^4$ cm^{-1} . The appearance at lower magnetic field of another paramagnetic center with $g=2.953(1)$ and $\Delta H=700(3)$ Gs at room temperature has been reported for $Mg_2InV_3O_{11}$. The second type of paramagnetic centers could be formed through the replacement of magnesium(II) and indium(II) ions [11]. The EPR spectrum of this center is strongly temperature dependent. For the first EPR spectrum only the intensity increases with decreasing temperature, while in the second case considerable shifts of the resonance lines are recorded. Comparison with a $CuSO_4$ reference sample allowed estimating that about 0.017% of the total vanadium ions are EPR active. Oxygen deficiency has been reported to vary essentially depending on the preparation conditions of these systems, whose physical properties could change strongly [15]. The EPR line that is centered at $g_{eff} \sim 2$ could arise from VO^{2+} vanadyl ions and is one order lower at liquid helium temperature [7]. EPR measurements of In_2O_3 showed three different paramagnetic centers [16]. The EPR spectra exhibit two broad asymmetric signals characterized by axial symmetry, poorly resolved hyperfine splitting and a sharp isotropic line. It has been proposed that indium(II) ions correspond to the electron configuration ($4d^{10}5s^1$ or $4d^95s^2$) with axial symmetry in an octahedral crystalline field. The hyperfine nuclear interaction with the nearest-neighbor ^{113}In or ^{115}In nuclei ($I=9/2$) is also detectable and can be resolved into 10 (2I+1) components. It could be attributed to the presence of electronic and 'hole' centers (F-centers, In^{2+}), and thus important for their transport properties.

Figure 2 shows the normalized temperature dependence of the resistivity for the two multicomponent vanadate oxide compounds $Zn_2InV_3O_{11}$ and $Co_2InV_3O_{11}$. Both compounds exhibit semiconducting behavior. Replacement of the non-magnetic Zn(II) cations with magnetic Co(II) ions results in a significant drop of the electrical conductivity, over four times, and a marked variation of the activation energy. The activation energies were determined to be $E_a=0.43(3)$ eV at $T<180$ K and $E_a=0.18$ eV at $T>200$ K for $Zn_2InV_3O_{11}$, in contrast to the value of $E_a=0.35$ eV derived at high temperatures for $Co_2InV_3O_{11}$. This behavior suggests that the concentration of charge carriers changed substantially upon replacement of Co(II) with Zn(II) ions, correlating with the increase of vanadium ions at the lower oxidation state derived by the EPR analysis. It is well known that a very good insulator with energy gap of 7.6 eV becomes semiconducting after introducing a low concentration of trivalent ions [17]. Indium oxide has been found to be a n -type semiconductor over a wide temperature range, while its electrical resistivity at room temperature is of the order of $\rho=10$ $\Omega \cdot cm$ with an activation energy of 1.55 eV [18]. The electrical properties of In_2O_3 were found to vary strongly with molybdenum doping, where the resistivity could decrease down to 2×10^{-4} $\Omega \cdot cm$ [19]. The carrier concentration increases with increasing molybdenum doping to a maximum value of $6.6 \cdot 10^{20}$ cm^{-3} .

The electrical conductivity (σ) depends on the concentration (N) and mobility (μ) of relevant free carriers as follows:

$$\sigma = N e \mu \quad (1)$$

where e is electron charge.

Previous conductivity measurements on the homologous compounds $Zn_kIn_{15-k}O_{45}$ ($k=3, 4, 5, 6, 7, 9, 11, 13, 15$) [20] have shown that the conductivity increases as k decreases due to the increase of both the carrier concentration and mobility. The lowest value of resistivity at room-temperature was reported for sample $Zn_3In_{12}O_{36}$ ($\rho=2.7 \times 10^3$ $\Omega \cdot cm$).

One possible mechanism for explaining electrical transport in amorphous indium oxide is the crossover from the Mott variable-range-hopping conductivity to the Coulomb-gap Efros-Shklovskii (ES) variable-range-hopping conductivity [21].

Oxygen deficiency processes in the multicomponent vanadate oxide (M(II)=Zn(II) and Co(II)) could provide carriers that lead to the increased electrical conductivity. The EPR measurements have shown a significant increase of the concentration of VO^{2+} vanadyl ions that could be responsible for the conductivity increase at two distinct temperature regions with different activation energies.

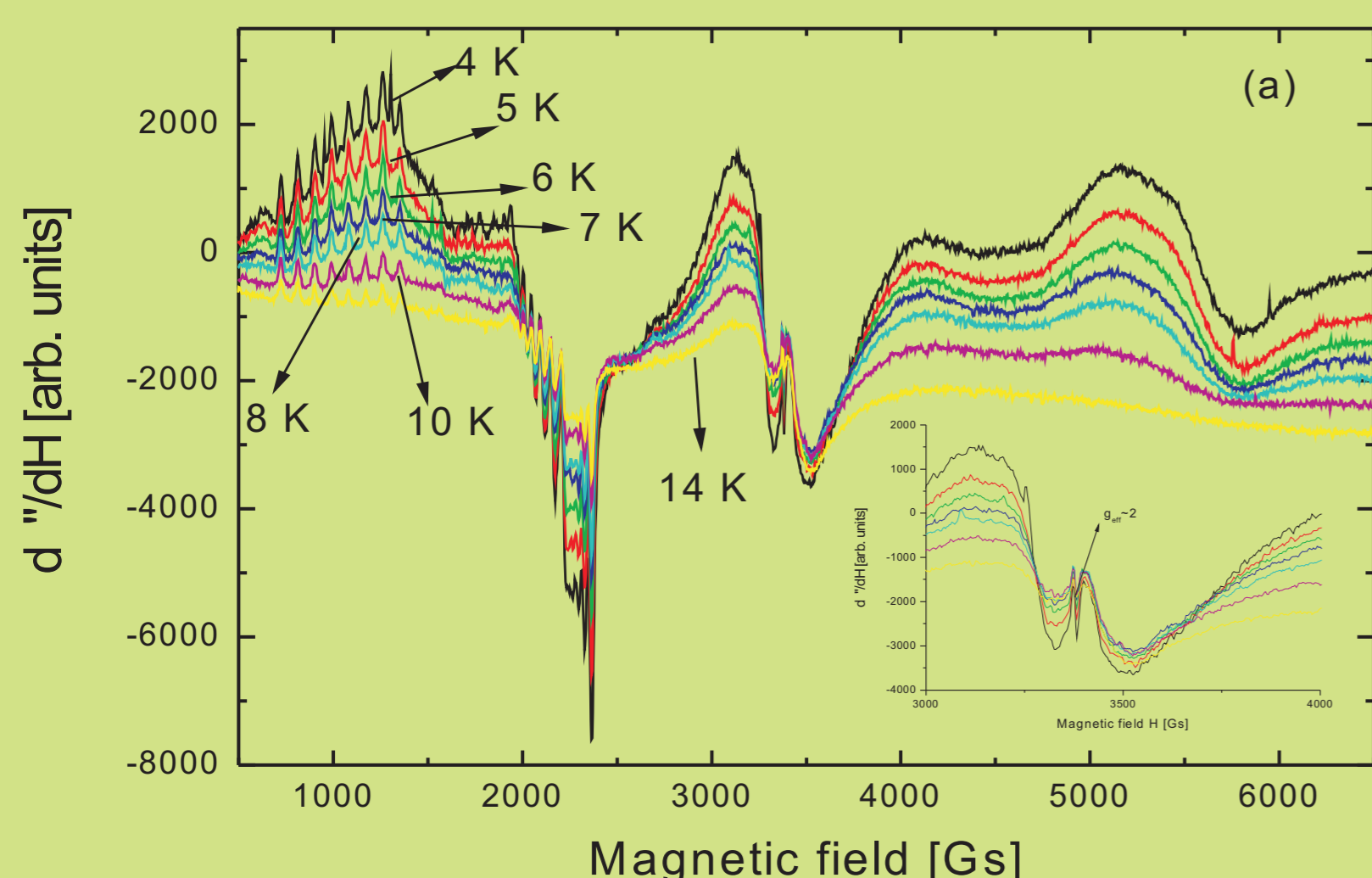


Figure 1 EPR spectra of the (a) $Co_2InV_3O_{11}$ and (b) $Zn_2InV_3O_{11}$ compounds.

