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Proceedings of the XIII National School of Superconductivity, Łądek Zdrój 2007

## Delocalization of the $\text{Cu}^{2+}$ Unpaired Electron on the Next Nearest Ligands in $\text{Sr}_2\text{Pd}_{0.99}\text{Cu}_{0.01}\text{O}_3$ Ceramics

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Supertransferred hyperfine interactions between the  $\text{Cu}^{2+}$  unpaired electron and the  $^{105}\text{Pd}$  nuclei in the  $\text{Sr}_2\text{Pd}_{0.99}\text{Cu}_{0.01}\text{O}_3$  ceramic were studied by the EPR method. The spectrum of isolated  $-\text{Pd}-\text{O}-\text{CuO}_2-\text{O}-\text{Pd}-$  units ( $g_{\parallel} = 2.280 \pm 0.001$ ;  $g_{\perp} = 2.040 \pm 0.001$ ;  $A_{\parallel} (^{63}\text{Cu}) = 13 \text{ mT} \pm 0.1$ ;  $A_{\parallel} (^{65}\text{Cu}) = 13.9 \pm 0.1 \text{ mT}$ ;  $A_{\perp} (^{63,65}\text{Cu}) = 0.0 \text{ mT}$ ) overlaps the signal from small groups of exchange coupled  $\text{Cu}^{2+}$  ions ( $g_{\parallel} = 2.278 \pm 0.002$ ;  $g_{\perp} = 2.041 \pm 0.001$ ). The isotropic contribution was shown to dominate in the Cu-Pd supertransferred interactions ( $A_{\parallel} (^{105}\text{Pd}) = A_{\perp} (^{105}\text{Pd}) = 1 \text{ mT} = a_{\text{iso Pd}}$ ).

PACS numbers: 33.15.Pw, 73.20.Jc, 76.30.Fc

### 1. Introduction

Delocalization of the unpaired electrons in magnets determines the cooperative interactions and the effects of the electron correlations. A special attention is paid to the study of the one-dimensional antiferromagnets, including  $\text{Sr}_2\text{MO}_3$  type ( $M = \text{metal}$ ) compounds [1, 2]. These materials allow investigation of the magnetic properties of both  $3d$ - and  $4d$ -elements. This study is a continuation of our earlier work in which we studied the crystals of the layer perovskite type [3]. In recent

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years the mixed  $\text{Sr}_2\text{Pd}_{1-x}\text{Cu}_x\text{O}_3$  and  $\text{Sr}_2\text{Cu}_{1-x}\text{Ni}_x\text{O}_3$  phases, being structural analogues of  $\text{Sr}_2\text{CuO}_3$ , have been studied by different methods [4–7]. Direct information about delocalization of the  $\text{Cu}^{2+}$  unpaired electron on the nearest cations can be obtained from electron paramagnetic resonance spectra. Here we report the EPR study of the super-transferred electron density in the  $\text{Sr}_2\text{Pd}_{0.99}\text{Cu}_{0.01}\text{O}_3$  ceramic material.

## 2. Experiment

Polycrystalline samples of the general formula  $\text{Sr}_2\text{Pd}_{1-x}\text{Cu}_x\text{O}_3$  (with  $x = 0.01$ ) were prepared according to the procedures described in literature [4]. The samples were oxygen-cooled in the final step.

$\text{Sr}_2\text{PdO}_3$  has an orthorhombic structure belonging to  $Immm$  space group [4, 8] with unit cell parameters  $a = 0.3985$  nm,  $b = 0.3539$  nm and  $c = 1.2847$  nm. This crystal structure is the same as that of  $\text{Sr}_2\text{CuO}_3$  and similar to that of  $\text{La}_2\text{CuO}_4$  in that it lacks oxygen ions between Cu ions along  $c$  axis. The differences in the ionic radius (0.064 and 0.057 nm for  $\text{Pd}^{2+}$  and  $\text{Cu}^{2+}$ , respectively) result in the crystal lattice deformation in  $\text{Sr}_2\text{Pd}_{1-x}\text{Cu}_x\text{O}_3$  solid solution.

EPR measurements were performed on an X-band RADIOPAN SE/X-2547 spectrometer with an Oxford ESR 900 flowing helium cryostat in the temperature range 4.2–300 K.

## 3. Results and discussion

The  $^{63,65}\text{Cu}^{2+} 3d^9$  ion has the electron spin  $S = 1/2$  and the nuclei spin  $I = 3/2$ . One can expect that the  $4d^8$  Pd ion in fourfold plane coordination is diamagnetic, however, the  $^{105}\text{Pd}$  isotopes (22.3% natural abundance) have the nuclear spin  $I = 5/2$  and their supertransferred hyperfine interaction with the  $3d$  copper electron allowed us to discover that its delocalization is not limited to nearest oxygen ions.

The room temperature EPR spectrum of the  $\text{Sr}_2\text{Pd}_{0.99}\text{Cu}_{0.01}\text{O}_3$  ceramic sample is shown in Fig. 1. Analysis of this anisotropic powder-type spectrum has revealed its hyperfine structure signals of the isolated  $\text{CuO}_4$  centers superimposed with the signal of the  $\text{Cu}^{2+}$  ions grouped in the small exchange clusters. The parameters of the single centres are:  $g_{\parallel} = 2.280 \pm 0.001$ ;  $g_{\perp} = 2.040 \pm 0.001$ ;  $A_{\parallel}(^{63}\text{Cu}) = 13 \text{ mT} \pm 0.1$ ;  $A_{\parallel}(^{65}\text{Cu}) = 13.9 \pm 0.1 \text{ mT}$ ;  $A_{\perp}(^{63,65}\text{Cu}) \leq 0.2 \text{ mT}$ . The cluster  $g$ -factors are:  $g_{\parallel} = 2.278 \pm 0.002$ ;  $g_{\perp} = 2.041 \pm 0.001$ . In the spectrum of the isolated complexes at 333 mT there is an “additional absorption peak”, which appears for the same ratio of  $g_i$  to  $A_i$  parameters. There are also some peculiarities significant for the spectrum analysis; these are the shoulders visible on the peak of the additional absorption and on the signal corresponding to the magnetic field  $\mathbf{B}$  direction perpendicular to the  $z$ -axis of the  $\text{CuO}_4$  unit and shoulders of each line of the hyperfine components of the spectrum corresponding to  $\mathbf{B}$  parallel to the  $z$ -axis. These additional signals are related to some interaction of the copper

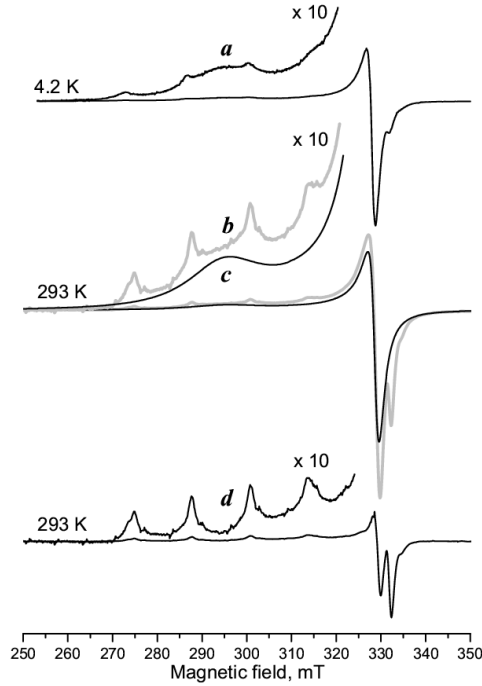


Fig. 1. EPR spectra of  $\text{Sr}_2\text{Pd}_{0.99}\text{Cu}_{0.01}\text{O}_3$  at 4.2 K (spectrum *a*) and 293 K,  $\nu = 9.3920$  (spectrum *b*); *c* is the fitting of the exchange narrowed signal from  $\text{Cu}^{2+}$  clusters ( $g_{\parallel} = 2.278 \pm 0.002$ ;  $g_{\perp} = 2.041 \pm 0.001$ ); *d* corresponds to the signal of the isolated  $-\text{Pd}-\text{O}-\text{CuO}_2-\text{O}-\text{Pd}-$  complexes and is a result of subtracting of the spectrum *c* from the experimental spectrum *b*.

unpaired electron with the magnetic moments of the  $^{105}\text{Pd}$  ion (ions) next near to copper ions.

All parameters of the EPR spectrum are not temperature dependent. Below 20 K, the intensity of individual  $\text{Cu}^{2+}$  spectra decreases due to saturation effects and the signal from the exchange clusters dominates, see Fig. 1.

The fitting procedure of this spectrum can be performed on the following conditions: (a) the  $g$ -factor has axial symmetry; (b)  $A_{\perp}(\text{Cu})$  value is no bigger than 0.05 mT; we accept  $A_{\perp}(\text{Cu}) = 0$ ; (c)  $A_{\parallel}(^{105}\text{Pd}) = A_{\perp}(^{105}\text{Pd}) = 1 \text{ mT} = a_{\text{iso Pd}}$ . Intensities of additional signals in the spectrum are determined by the abundance of  $^{105}\text{Pd}$  isotope (22.2%) and probability of various configurations of  $\text{Pd}^{2+}$  ions with  $I = 5/2$  around  $\text{Cu}^{2+}$  ions. The presence of one  $^{105}\text{Pd}$  results in the signal splitting into 6 lines of superhyperfine structure, interaction with two  $^{105}\text{Pd}$  ions leads to  $(2nI + 1) = 11$  components of the super-hyperfine structure with the intensities 1:2:3:4:5:6:5:4:3:2:1. We used these conclusions for modelling of the observed spectrum taking into account that  $^{65}\text{A}_{\text{Cu}}/^{63}\text{A}_{\text{Cu}}$  ratio is proportional to the gyromagnetic ratio of the nuclei  $^{65}\gamma_{\text{Cu}}/^{63}\gamma_{\text{Cu}} = 1.0701$  [9]. The parameters

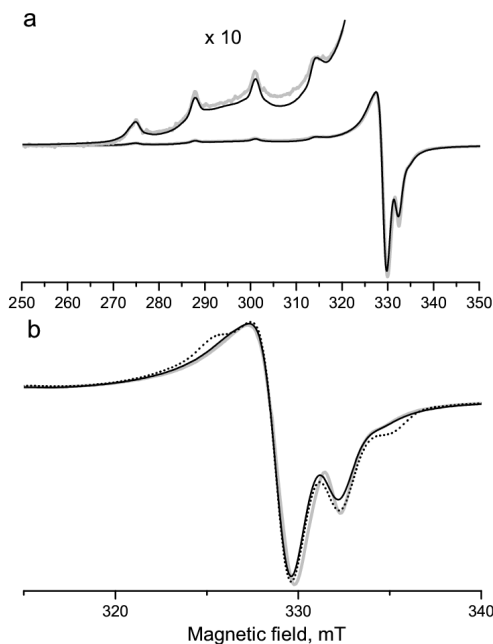


Fig. 2. Comparison of the experimental (gray line) and theoretical (black line) spectra. The latter is composed of the signal *b*, shown in Fig. 1, and the theoretical spectra of isolated  $\text{-Pd-O-CuO}_2\text{-O-Pd-}$  units generated by WINEPR SimFonia for the following parameters of spin Hamiltonian:  $g_{\parallel} = 2.28$ ;  $g_{\perp} = 2.04$ ;  $A_{\parallel}({}^{63}\text{Cu}) = 13.0$  mT;  $A_{\parallel}({}^{65}\text{Cu}) = 13.9$  mT;  $A_{\perp}({}^{63,65}\text{Cu}) = 0$  mT;  $A_{\parallel}({}^{105}\text{Pd}) = A_{\perp}({}^{105}\text{Pd}) = a_{\text{iso Pd}} = 1$  mT; (a) details of fitting of the part of spectrum corresponding to the centers with  $z$ -axis parallel to the magnetic field  $\mathbf{B}$ ; (b) details of the fitting of the part of spectrum corresponding to the centers with  $z$ -axis perpendicular to the magnetic field  $\mathbf{B}$ . The dotted line showing fitting for  $A_{\perp}({}^{105}\text{Pd}) = 12$  mT proves that the case of  $A_{\perp}({}^{105}\text{Pd}) > A_{\parallel}({}^{105}\text{Pd})$  is unacceptable.

obtained from the experiment and those used in the fitting procedure are presented in the caption to Fig. 2.

The most significant result of this fitting is the conclusion that the super-hyperfine splitting due to the  ${}^{105}\text{Pd}$  has isotropic character. The predominance of the isotropic contribution in the interaction of the copper electron with the palladium nucleus shows that the supertransferred hyperfine field arises as a result of the appearance of the spin density on  $s$ -orbitals of palladium. It is possible as a result of the total effect of polarization of the occupied inner  $1s$ – $4s$ -orbitals and the appearance of the spin density on the outer  $5s$ -orbital of Pd ion.

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