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## The Origin of EPR Signals in SrCuO<sub>2</sub> Ceramics

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The origin and thermal evolution of the EPR signals in SrCuO<sub>2</sub> ceramics are studied. It has been shown that the EPR signals observed in this ceramic material are due to contamination with other phases. The axial signal is due to SrCu(OH)<sub>4</sub>·H<sub>2</sub>O, which is a product of water reactions with SrCuO<sub>2</sub>.

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### 1. Introduction

SrCuO<sub>2</sub> and Sr<sub>2</sub>CuO<sub>3</sub> compounds are recognised as ideal systems of 1D  $S = 1/2$  antiferromagnetic Heisenberg chains with the exchange interaction  $J$  estimated to be about 2200 K [1]. They should be EPR silent but EPR signals have been observed in the SrCuO<sub>2</sub> and Sr<sub>2</sub>CuO<sub>3</sub> ceramics [2, 3]. These signals have been usually assigned to structural defects breaking the antiferromagnetic interactions [2]. However, it has been established that exposition of Sr<sub>2</sub>CuO<sub>3</sub> to humid air results in its decomposition [4, 5] and the decomposition products were identified by X-ray diffraction (XRD) phase analysis. The orthorhombic EPR signal of one of these products, namely Sr<sub>2</sub>Cu(OH)<sub>6</sub> [5] is identical as that observed in Sr<sub>2</sub>CuO<sub>3</sub> ceramics. A similar study of SrCuO<sub>2</sub> has shown that this compound is much less sensitive to humid air and in [4] there is no information about XRD identification of any traces of SrCuO<sub>2</sub> reaction with water. Nevertheless, results of [4] have put into the question the hypothesis that the EPR signal in SrCuO<sub>2</sub> ceramic can be connected with structural defects. Additional hint for us was that

in the samples of SrCuO<sub>2</sub> doped with K<sup>+</sup> and Li<sup>+</sup> and stored for some years we have observed a signal identical to that observed in Sr<sub>2</sub>CuO<sub>3</sub> [3].

The paper presents results concerning the influence of the presence of the admixture phases and the humid air on the EPR spectra of SrCuO<sub>2</sub>.

## 2. Experimental

### 2.1. Synthesis

Two SrCuO<sub>2</sub> samples were prepared by a conventional solid-state reaction technique from mixtures of high purity raw materials: CuO and SrCO<sub>3</sub> (Specpure, Johnson, Matthey Chemicals Limited). Two types of samples were prepared. To get sample (A) the compounds CuO and SrCO<sub>3</sub> were mixed in appropriate proportions to obtain the stoichiometric material. The powder mixture was calcined initially in air at 1223 K for 10 hours, then the material was reground, pressed into tablets and sintered in air at 1223 K for 20 hours. The samples were then cooled in furnace to 773 K and quenched to room temperature. A similar procedure, but for a different nominal ratio of components Sr : Cu = 1.08 : 0.92 was used to obtain Sr<sub>1.08</sub>Cu<sub>0.92</sub>O<sub>2</sub> labelled as sample (B). The samples were sintered in air, and then cooled in furnace to room temperature.

### 2.2. Structural analysis

Powder X-ray diffraction patterns were obtained with a DRON-2 diffractometer using Fe K<sub>α</sub> radiation with β filter. The data were analysed by the full profile analysis of Rietveld method. The program MAUDI.9992 [6] was used.

### 2.3. EPR study

The EPR spectra were recorded with a RADIOPAN SE/X-2547 spectrometer with 100 kHz magnetic modulation, at room temperature and at 77 K.

Fresh, as-prepared samples were studied not later than 2–3 hours after getting them out from the furnace. In this time samples were cut to small pieces, which were placed in the tubes. All handling was done in the air. Measurements were also carried on after exposition of the samples to steam and hot water and after consecutive steps of the thermal treatment.

## 3. Results

### 3.1. Structural analysis

Results of the structural analysis are presented in the Table. In sample (A) admixtures of 6.3 molar % of Sr<sub>14</sub>Cu<sub>24</sub>O<sub>41</sub> and 1.4 molar % of Sr<sub>2</sub>CuO<sub>3</sub> were found. In sample (B) 18.3 molar % of Sr<sub>2</sub>CuO<sub>3</sub> and some small amounts of unidentified phases were detected.

TABLE

Results of the structural phase analysis.

Compound	Sample (A)				Sample (B)			
	Molar %	<i>a</i> [Å]	<i>b</i> [Å]	<i>c</i> [Å]	Molar %	<i>a</i> [Å]	<i>b</i> [Å]	<i>c</i> [Å]
SrCuO <sub>2</sub>	92.3	3.571	16.323	3.911	79.6	3.571	16.322	3.911
Sr <sub>2</sub> CuO <sub>3</sub>	1.4	3.930	3.508	12.837	18.3	3.913	3.502	12.702
Sr <sub>14</sub> Cu <sub>24</sub> O <sub>41</sub>	6.3	11.475	13.345	27.656				
Unidentified					2.1			

## 3.2. EPR study

The spectra shown in Fig. 1 were recorded for the “as-prepared samples”. An axial spectrum (*a*) of a fresh (A) sample is typical of the SrCuO<sub>2</sub> compound with  $g_{\parallel} = 2.259$  and  $g_{\perp} = 2.055$ . In the spectrum (*b*) of the fresh sample (B) an

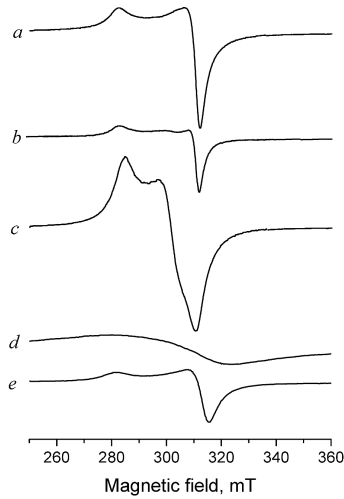


Fig. 1. The spectra of as-prepared samples; *a* — fresh sample (A) SrCuO<sub>2</sub>; *b* — fresh sample (B) Sr<sub>1.08</sub>Cu<sub>0.92</sub>O<sub>2</sub>; *c* — the same sample (B) after 20 h storing in air; *d* — RT spectrum of the sample (A1) stored in the closed container for 2 months; *e* — the spectrum of the (A1) sample at 77 K.

admixture of the orthorhombic signal is clearly seen. After 20 hours in air the axial signal in this sample has been transformed into the orthorhombic spectrum (*c*) with  $g_x = 2.245$ ,  $g_y = 2.115$ , and  $g_z = 2.051$  and with traces of the axial signal. The spectrum (*d*) was recorded at RT for a sample (A) stored, in a small closed container under dry air for two months and marked as (A1). No traces of the axial signal were visible. The sample (A1) with the broad (*d*) spectrum recorded at 77 K exhibits the axial spectrum (*e*) with  $g_{\parallel} = 2.277$  and  $g_{\perp} = 2.045$ .

Exposition of the fresh  $\text{SrCuO}_2$  samples to humid air and to water results in a strong increase in the intensity without changing the form of the spectra (or, in the case of the stored sample (A1), in the appearance of the axial signal). A rapid, steam induced increase in the axial spectrum intensity was earlier reported [2]. In the case of a fresh as-prepared sample (B) the exposition to steam causes an increase in the axial and orthorhombic signals to the same degree and the spectrum shape remains the same as the spectrum *b* in Fig. 1.

Small ceramic pieces of the studied ceramics, with a strong water-induced axial signal and a mass of about 20 mg were immersed in silicone oil for isolation from the air. These samples were gradually annealed in the range of 383–453 K. At each temperature they were kept for 15 minutes, took out from the oven and cooled down to room temperature and then their EPR spectra were recorded. The results obtained for sample (A) are shown in Fig. 2. Heating the sample to the 110°C (383 K) results in a small increase in the axial spectrum intensity, but starting from 120°C (393 K) up to 180°C (453 K) a gradual transformation of the axial into the orthorhombic signal is observed. Additional heating at this temperature completes the process of transformation and the pure orthorhombic spectrum is observed.

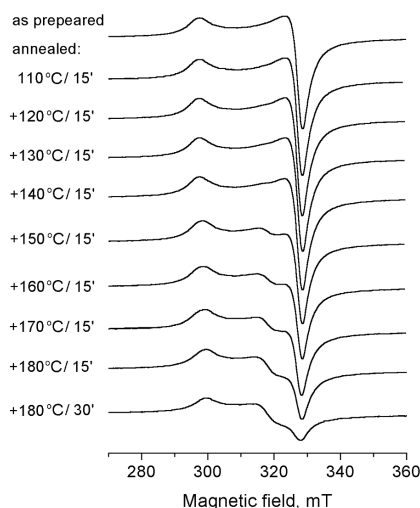


Fig. 2. The evolution of the water induced spectrum of sample (A) annealed at different temperatures.

For heating to higher temperatures the samples were isolated from humid air by a thick layer of  $\text{Al}_2\text{O}_3$  powder. Annealing at temperatures above 250°C (523 K) affected the orthorhombic spectra, whose intensity gradually decreased. The process was similar for  $\text{SrCuO}_2$  (A) and  $\text{Sr}_{1.08}\text{Cu}_{0.92}\text{O}_2$  (B) samples. After the final heating at 350°C (623 K) only featureless broad lines are observed at room temperature (see Fig. 3). These lines transform with temperature decreasing. At

77 K the axial spectrum with  $g_{\parallel} = 2.277$  and  $g_{\perp} = 2.045$  is observed for the sample (A). The transformation of the signal of sample (B) is different and only a change in its linewidth from about 30 mT at RT to about 19 mT at 77 K (Fig. 3b) is observed.

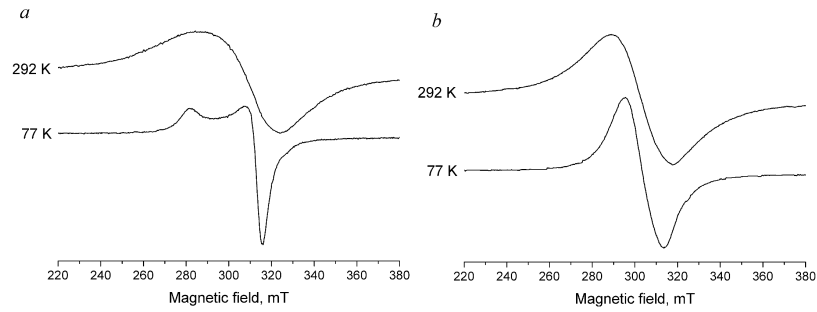


Fig. 3. The spectra of the samples annealed at 350°C; (a) a broad EPR signal of a sample (A) transforms at 77 K to the axial spectrum; (b) a broad EPR signal of CuO in a sample (B) at 77 K becomes narrowed indicating the nanosized dimensions of CuO grains.

Exposition of the thermally treated samples with spectra presented in Fig. 3 to humid air, hot steam or water results in the appearance of orthorhombic spectrum. The presence of the axial spectrum often treated as the characteristic EPR spectrum of SrCuO<sub>2</sub> ceramics can be detected only by the line shape analysis.

#### 4. Discussion

Sr<sub>14</sub>Cu<sub>24</sub>O<sub>41</sub> identified as the admixture phase in the sample (A) exhibits a strong EPR signal [7] with  $g_{\parallel} = 2.28 \pm 0.03$  and  $g_{\perp} = 2.04 \pm 0.02$ . The linewidth of the EPR signal of the single Sr<sub>14</sub>Cu<sub>24</sub>O<sub>41</sub> crystal, measured for the magnetic field along the narrower perpendicular direction, is about 27 mT at RT and decreases to about 3 mT at 77 K. The admixture of 6% should result in a noticeable EPR signal. The principal values of  $g$ -factor, measured at 77 K and differences in the linewidth at RT and 77 K indicate that the EPR signal of the stored sample (A1) and the signal in samples (A) after annealing at high temperatures (Fig. 3a) can be ascribed to the admixture of Sr<sub>14</sub>Cu<sub>24</sub>O<sub>41</sub> phase.

It was shown [2] and our observations have confirmed this that the intensity of the axial signal observed for SrCuO<sub>2</sub> is sensitive to the moisture and increases strongly after direct exposition to water. We have shown also that the axial signal transforms with temperature to the orthorhombic one, which was assigned to Sr<sub>2</sub>Cu(OH)<sub>6</sub> [4]. It suggests that the axial signal is due to another hydroxide of strontium and copper. The best candidate is SrCu(OH)<sub>4</sub>·H<sub>2</sub>O, which was studied as a possible precursor of the SrCuO<sub>2</sub> phase [8, 9]. Its EPR spectrum is typical

of the square-planar coordination of  $\text{Cu}^{2+}$  ion [10] with  $g_{\parallel} = 2.26$  and  $g_{\perp} = 2.06$  parameters very close to those of the  $\text{SrCuO}_2$  ceramics. The thermal decomposition of  $\text{SrCu}(\text{OH})_4 \cdot \text{H}_2\text{O}$  was studied [9] by differential scanning calorimetry (DSC) and XRD analysis was used for the products identification. It was found that in the temperature range of  $120\text{--}180^\circ\text{C}$  ( $393\text{--}453\text{ K}$ ) 2 molecules of  $\text{SrCu}(\text{OH})_4 \cdot \text{H}_2\text{O}$  loose 3 molecules of  $\text{H}_2\text{O}$  and decompose into  $\text{Sr}_2\text{Cu}(\text{OH})_6$  and  $\text{CuO}$ . Above  $250^\circ\text{C}$  next steps of dehydration were observed yielding  $\text{Sr}(\text{OH})_2$  and  $\text{CuO}$ . The final weight loss observed between  $350$  and  $470^\circ\text{C}$  involved the partial back reaction of strontium hydroxide and copper oxide to yield  $\text{Sr}_2\text{CuO}_3$ . The excess amount of  $\text{CuO}$  was detected in the sample [9].

The above-described transformations are fully consistent with the observed by us evolution of EPR spectra with temperature. The axial signal of  $\text{SrCu}(\text{OH})_4 \cdot \text{H}_2\text{O}$  transforms between  $120^\circ\text{C}$  ( $373\text{ K}$ ) and  $180^\circ\text{C}$  ( $553\text{ K}$ ) into the orthorhombic one of  $\text{Sr}_2\text{Cu}(\text{OH})_6$ . This compound decomposes to the diamagnetic  $\text{Sr}(\text{OH})_2$  and  $\text{CuO}$ , whose signal is very broad. As the  $\text{CuO}$  is the only paramagnetic product of thermal decomposition the broad signal observed for sample (B) annealed at  $623\text{ K}$  (Fig. 3b) should be assigned to  $\text{CuO}$ . In the crystalline  $\text{CuO}$  with Néel temperature  $T_N = 230\text{ K}$  lowering temperature down to  $77\text{ K}$  results in the strong increase in the resonant linewidth and the EPR spectra is hardly detectable. However, in nano-powders a shift of the Néel temperature down to  $40\text{ K}$  is observed [11]. Therefore, the observed decrease in the linewidth (Fig. 3b) suggests the nanosize dimensions of the  $\text{CuO}$  crystallites.

The signal with orthorhombic symmetry (Fig. 1c) observed in samples (B) kept in air is a result of an admixture of  $19.6$  molar % of  $\text{Sr}_2\text{CuO}_3$  phase. As this phase is more reactive than  $\text{SrCuO}_2$  on the beginning of water decomposition of the sample the signal of  $\text{Sr}_2\text{Cu}(\text{OH})_6$  predominates the signal of  $\text{SrCu}(\text{OH})_4 \cdot \text{H}_2\text{O}$ . However, when the whole surface phase of  $\text{Sr}_2\text{CuO}_3$  has been already decomposed, the less effective decomposition of  $\text{SrCuO}_2$  phase results in an increase in the axial signal intensity. The back reaction and  $\text{Sr}_2\text{CuO}_3$  synthesis can explain the appearance of the orthorhombic signals in the samples exposed to water earlier subjected to the thermal treatment. This compound reacts readily with moisture and yields the orthorhombic signal. At the same time a layer of the  $\text{CuO}$  dispersed on the ceramic surface together with  $\text{Sr}_2\text{CuO}_3$  and  $\text{Sr}_2\text{Cu}(\text{OH})_6$  protect the surface and the bulk of  $\text{SrCuO}_2$  from contact with water, so the axial signal becomes only an admixture to the orthorhombic one.

## 5. Conclusions

The EPR signals observed in the  $\text{SrCuO}_2$  ceramics are due to the contamination with other phases and decomposition of the ceramic surface caused by water.

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