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SOME ELECTRONIC PROPERTIES OF $Sr_{1-x}A_xCuO_{2+\delta}$ WHERE A = La, K, AND Ca

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The electronic properties of $Sr_{1-x}A_xCuO_{2+\delta}$ (A = La, K, Ca) were examined. The crystal structure of the synthesized compounds was identified as orthorhombic with some admixture of tetragonal phase. For $Sr_{1-x}La_xCuO_{2+\delta}$ the insulator–metal like transition was observed with increasing La content. The $d_{x^2-y^2}$ ground state of Cu ions was deduced from electron spin resonance measurements. The electronic state of Cu ions and their surrounding local symmetry was also found to be La and oxygen content dependent.

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1. Introduction

Several papers have been recently devoted to superconducting $Sr_{1-x}A_xCuO_{2+\delta}$ (A=Ba, Nd, La, Pr, Sm) compounds [1]. It was demonstrated that when synthesized under high pressure these compounds crystallize in a layered tetragonal structure built of alternately stacked A and $[CuO_2]_\infty$ layers. On the other hand, no results are known on $Sr_{1-x}A_xCuO_{2+\delta}$ with $SrCuO_2$ ambient pressure pattern structure. $SrCuO_2$ crystallizes in orthorhombic structure [2] which consists of alternating planes of double CuO chains and double SrO rock salt sheets. Although these structures are not closely related to that of high-T_c superconducting cuprates it is interesting to explore their electronic properties with respect to substitutions in the cation sublattice. In this communication we report our results of investigation of $Sr_{1-x}A_xCuO_{2+\delta}$ (A = La, K, Ca) compounds.

2. Experimental

The samples were sintered by conventional ceramic method at temperatures close to 1250 K. The starting materials (all of spectral purity except K_2CO_3 which was pure for analysis) were powders of CuO, $SrCO_3$ and La_2O_3, $CaCO_3$, and K_2CO_3 for $Sr_{1-x}A_xCuO_{2+\delta}$ with A = La, Ca, and K, respectively. The products were examined by powder X-ray diffraction (XRD) using Cu K_α radiation.

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Standard four probe method was applied to resistivity measurements. The ESR experiments were performed using standard X-band RADIOPAN-SE/X 2547 spectrometer with magnetic field modulation of 100 kHz and a home-made Q-band spectrometer. A digital NMR magnetometer JTM-247 RADIOPAN was used for magnetic induction and ESR line width measurements.

3. Results and discussion

XRD patterns for synthesized compounds were in majority indexed accordingly to $SrCuO_2$ host structure. However, some admixtures of tetragonal phase were also observed.

The measured temperature dependencies of resistivity (ρ) indicate that $Sr_{0.5}Ca_{0.5}CuO_{2+\delta}$ and $Sr_{1-x}K_xCuO_{2+\delta}$ compounds are insulators or semiconductors, showing thermally activated conduction with activation energies of 0.15 eV and 0.12 eV, respectively. The $\rho(T)$ dependencies for $Sr_{1-x}La_xCuO_{2+\delta}$ are shown in Fig. 1. Gradual changes in ρ values and $\rho(T)$ slopes with increasing La content

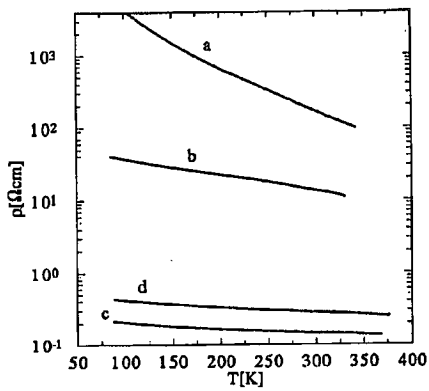

Fig. 1. The temperature dependence of the resistivity in $Sr_{1-x}La_xCuO_{2+\delta}$. The curves a, b, c, and d correspond to $x = 0.1, 0.2, 0.3$, and 0.5, respectively.

are seen. For $0.2 > x > 0.3$ the transition from insulating to metallic conductivity seems to occur. The remaining slight negative slope in $\rho(T)$ may be either associated with a disorder induced localization or indicates that only the proximity of the insulator–metal transition is achieved.

The g-factors and the crystal field splitting parameters (CFSP) calculated from the ESR spectra are collected in Table. The ESR spectra in all cases can be attested to the Cu^{2+} ions. However, the environment of the ions is found to be dependent both on a sample composition and on a sample preparation. In the case of $Sr_{0.5}K_{0.5}CuO_{2+\delta}$ and $Sr_{0.5}Ca_{0.5}CuO_{2+\delta}$ grounded samples the local symmetry of the Cu^{2+} ions can be ascribed to uniaxial one. The same local symmetry can be deduced for La substituted ($x = 0.1$ and 0.2) $SrCuO_2$ pellet samples. The axial symmetry of g-factor with rather small orthorhombic distortion observed in grounded $Sr_{1-x}La_xCuO_{2+\delta}$ samples indicates that the ESR signals originate from planar fourfold coordinated Cu^{2+} ions. From the shape of the ESR spectra,

TABLE

Results of ESR measurements.

Compound	Sample type	X-band		Q-band
		g-factor[a]	CFSP [cm^{-1}]	g-factor[a]
$K_{0.5}Sr_{0.5}CuO_{2+\delta}$	grounded	$g_{\parallel} = 2.226$ $g_{\perp} = 2.035$	$\Delta_0 = 29647$ $\Delta_1 = 50703$	$g_{\parallel} = 2.253$ $g_{\perp} = 2.058$
$Ca_{0.5}Sr_{0.5}CuO_{2+\delta}$	grounded	$g_{\parallel} = 2.250$ $g_{\perp} = 2.043$	$\Delta_0 = 26774$ $\Delta_1 = 40737$	$g_{\parallel} = 2.267$ $g_{\perp} = 2.049$
$La_{0.5}Sr_{0.5}CuO_{2+\delta}$	pellet			
$La_{0.5}Sr_{0.5}CuO_{2+\delta}$	grounded	$g_{\text{eff}} = 2.023$		$g_{\text{eff}} = 2.27$
$La_{0.4}Sr_{0.6}CuO_{2+\delta}$	pellet			$g_{\text{eff}} = 2.01$
$La_{0.4}Sr_{0.6}CuO_{2+\delta}$	grounded	$g_{\parallel} = 2.230$ $g_{\perp} = 2.032$	$\Delta_0 = 29126$ $\Delta_1 = 55825$	$g_1 = 2.047$ $g_2 = 2.102$ $g_3 = 2.262$
$La_{0.3}Sr_{0.7}CuO_{2+\delta}$	pellet			
$La_{0.3}Sr_{0.7}CuO_{2+\delta}$	grounded	$g_{\text{eff}} \approx 2$		$g_{\text{eff}} = 2.075$ $g_{\text{eff}} = 2.078$
$La_{0.2}Sr_{0.8}CuO_{2+\delta}$	pellet	$g_{\parallel} = 2.245$ $g_{\perp} = 2.032$	$\Delta_0 = 27326$ $\Delta_1 = 55825$	
$La_{0.2}Sr_{0.8}CuO_{2+\delta}$	grounded	$g_1 = 2.037$ $g_2 = 2.075$ $g_3 = 2.236$		$g_1 = 2.047$ $g_2 = 2.08$ $g_3 = 2.242$
$La_{0.1}Sr_{0.9}CuO_{2+\delta}$	pellet	$g_{\parallel} = 2.293$ $g_{\perp} = 2.081$		$g_{\parallel} = 2.264$ $g_{\perp} = 2.047$
$La_{0.1}Sr_{0.9}CuO_{2+\delta}$	grounded	$g_1 = 2.037$ $g_2 = 2.075$ $g_3 = 2.242$		$g_1 = 2.054$ $g_2 = 2.108$ $g_3 = 2.256$

[a] $|\Delta g| = 0.008$ was estimated as the upper bound of g-factor error.

calculated values of g-factor ($g_{\parallel} > g_{\perp} > g_e$), and the G parameter value the $d_{x^2-y^2}$ state can be deduced as the ground state of d^9 configuration of Cu.

The mechanism driving the orthorhombic distortion in grounded samples is not clear. Some changes in oxygen content are possible due to the sample grounding processed in the air. The tendency to oxygen incorporation may reflect some lattice instability against La substitution. Sr substitution with La may first symmetrize Cu surrounding toward uniform square ($g_{\parallel} - g_{\perp}$ for $x = 0.1$ and 0.2 is greater than that found for $x = 0.4$) and when oxygen is incorporated the Cu coordination distorts to orthorhombic symmetry. A systematic investigation of the effect of oxygen treatment on transport properties and Cu electron state are desirable for detailed

explanation of these features. For La rich pellet samples ($0.3 < x < 0.5$) ESR signal is hardly observed. After grounding the signal intensity slightly increases and consists of the broad line which enables us to determine only the effective value of g-factor. Actually, the origin of the broad ESR lines is not resolved. An increase in covalency of Cu–O bonds in metallic $Sr_{1-x}La_xCuO_{2+\delta}$ samples, and therefore more anionic character of Cu electron state, may be suggested as qualitative explanation of the observed line broadening [3].

In conclusion, we have demonstrated that Sr substitution with La converts insulating properties of $SrCuO_2$ to metallic. ESR measurements on pellet and grounded samples indicate that oxygen content strongly affects electronic state of Cu^{2+} ions. A more complete identification of $Sr_{1-x}La_xCuO_{2+\delta}$ phase as well as farther investigation of its electronic properties are still in progress.

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