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MÖSSBAUER STUDIES OF ^{57}Co -DOPED LAYERED PEROVSKITES *

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Mössbauer spectra of ^{57}Co -doped polycrystalline or single-crystal samples of layered perovskites La_2MO_4 ($M = \text{Cu, Co, Ni}$) and R_2CuO_4 ($\text{R} = \text{Nd, Eu, Gd}$) were recorded at room temperature and below. Of the samples studied, only La_2CuO_4 shows a widely separated doublet at room temperature and a single clearly resolved sextet well below T_N .

1. Introduction

The layered perovskite La_2CuO_4 is the parent compound from which the first high- T_c superconductors were obtained [1] by doping with divalent elements. La_2CuO_4 is orthorhombic at and below room temperature [2]. Oxygen-deficient $\text{La}_2\text{CuO}_{4-y}$ is antiferromagnetic with T_N as high as 328 K [2,3], while oxygen-rich $\text{La}_2\text{CuO}_{4+y}$ is superconducting with $T_c \sim 30$ K [4]. La_2CoO_4 is orthorhombic at room temperature and becomes tetragonal below ~ 135 K; it becomes antiferromagnetic below about 275 K [5]. La_2NiO_4 is very sensitive to oxygen content, the stoichiometric compound being orthorhombic and not magnetically ordered between 95 K and 4 K [6] while $\text{La}_2\text{NiO}_{4.05}$ undergoes a tetragonal to orthorhombic transition in cooling below about 240 K and becomes antiferromagnetic below 70 K [7].

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Recently the layered perovskites $\text{R}_2\text{CuO}_{4-y}$, where $\text{R} = \text{Pr}, \text{Nd}, \text{Sm}$ [8] or Eu but not Gd [9], have been found to be electron-type superconductors below about 20 K when 15% of R is replaced with tetravalent Ce or Th . The parent compounds $\text{R}_2\text{CuO}_{4-y}$ are tetragonal and semiconductorlike, and in muon spin rotation experiments reveal static magnetic order of Cu moments below 300 K [10]. Antiferromagnetic ordering of Cu in R_2CuO_4 below room temperature has been suggested by susceptibility measurements for $\text{R} = \text{Eu}$ [11] and Gd [12]. The compounds $\text{R}_2\text{CuO}_{4-y}$, where $\text{R} =$ light rare earth element Pr through Gd , differ from $\text{La}_2\text{MO}_{4-y}$ in that the former have oxygen atoms square-planar coordinated about Cu , while in the latter oxygen atoms are octahedrally coordinated about Cu [5,8,13].

The present work undertakes Mössbauer studies of ^{57}Co -doped [16] polycrystalline or single-crystal samples of layered perovskites $\text{La}_2\text{MO}_{4-y}$ ($\text{M} = \text{Cu}, \text{Co}, \text{Ni}$) and R_2CuO_4 ($\text{R} = \text{Nd}, \text{Eu}, \text{Gd}$).

2. Experimental results

Polycrystalline samples of $\text{La}_2\text{MO}_{4-y}$ and R_2CuO_4 were made by mixing stoichiometric amounts of the constituents by co-precipitation and by repeated grinding and firing [14]. Samples were cooked at 500°C overnight, in flowing helium gas to produce the oxygen-deficient form, or in air to produce the stoichiometric form. X-ray powder diffraction showed the samples to be single-phase. Thin, platelike single-crystal samples were grown from PbO - and CuO -based fluxes; the tetragonal c -axis was perpendicular to the thin face [11,12].

For Mössbauer source experiments, carrier-free ^{57}Co was deposited on one face of the single-crystal sample or on a disk made by compressing a polycrystalline sample; after repeating the final anneal such sources were used with a 0.3

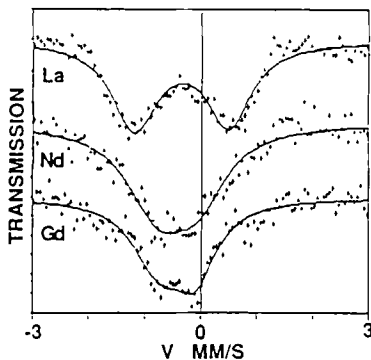


Fig. 1. Mössbauer spectra of single-crystal samples of R_2CuO_4 at 295 K.

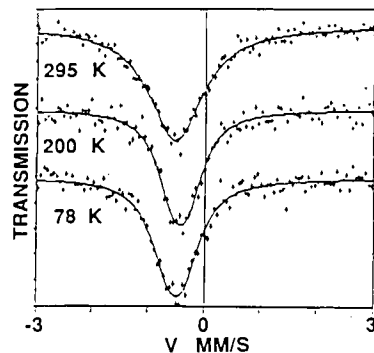


Fig. 2. Mössbauer spectra of $\text{La}_2\text{CoO}_{4-y}$ versus T .

Table 1

Mössbauer data for ^{57}Co -doped perovskites. T is the sample temperature. Sample form is single crystal (SC) or polycrystalline (PC); absorber is PFC unless indicated ^{ss}. In mm/s, δ is the isomer shift relative to $\alpha\text{-Fe}$, Γ is the FWHM for all lines in the spectrum, and Δ is the splitting of the doublet or ΔE_Q . Error in the least significant digit is given in ().

Sample	Form	T (K)	δ	Γ	Δ^a	H (kOe)
La_2CuO_4	SC	295	-0.30 (5)	0.96	1.68 (5)	
$\text{La}_2\text{CuO}_{4-y}$	PC	295 ^b	-0.30 (1)	0.44	1.76 (2)	
		100 ^b	-0.19 (1)	0.34	-0.97 (1)	434 (5)
$\text{La}_2\text{CoO}_{4-y}$	PC	295	-0.48 (5)	1.2	0.0 (4)	
		200	-0.39 (5)	0.67	0.29 (5)	
		78	-0.46 (5)	0.76	0.29 (5)	
$\text{La}_2\text{NiO}_{4-y}$	PC	295	-0.51 (5)	0.71	0.61 (5)	
Nd_2CuO_4	SC	295	-0.38 (5)	1.2	0.7 (1)	
Eu_2CuO_4	SC	295	-0.30 (5)	0.82	0.65 (5)	
Eu_2CuO_4	PC	295 ^{ss}	-0.34 (5)	0.64	0.66 (5)	
		78 ^{ss}	-0.72 (5)	0.64	0.30 (5)	370 (10)
			-0.75 (5)	0.64	0.78 (5)	
Gd_2CuO_4	SC	295	-0.40 (5)	1.0	0.66 (5)	
Gd_2CuO_4	PC	295	-0.51 (5)	0.24	0.66 (5)	
		200	-0.46 (5)	0.24	0.53 (5)	
		180 ^{ss}	-0.72 (5)	0.64	0.04 (5)	290 (10)
			-0.59 (5)	0.64	0.07 (5)	220 (10)
		78 ^{ss}	-0.68 (5)	0.64	0.38 (5)	510 (10)
		-0.68 (5)	0.64	0.32 (5)	360 (10)	
			0.14 (5)	0.64	1.31 (5)	

^a Sign not determined where not explicitly given.

^b Ref. [14].

mg/cm² ^{57}Fe enriched potassium ferrocyanide (PFC) or stainless steel (SS) absorber at room temperature.

Mössbauer spectra are given in figs. 1 and 2, and the data are presented in table 1. Spectra are fitted with a doublet for 295 K, and for R_2CuO_4 (R = Eu, Gd) below 200 K, with a doublet and 1 or 2 sextets.

3. Discussion

La_2MO_4 (M = Cu, Co, Ni) have similar lattice constants and Cu-O octahedra; R_2CuO_4 (R = Nd, Eu, Gd) have larger c/a ratios and Cu-O squares. Room-temperature Mössbauer spectra of ^{57}Co -doped samples are each fitted with a doublet, but the splitting is sizable (> 1 mm/s) only for La_2CuO_4 . If in La_2CuO_4 this is interpreted as quadrupole splitting, then the ^{57}Fe probe experiences much greater electric field gradient in La_2CuO_4 than in R_2CuO_4 . This might be due to the difference in oxygen coordination or to the difference in c/a ; in either case one would have expected sizable splitting in La_2MO_4 (M = Co, Ni) as well.

Comparison [14] of ^{57}Co - and ^{57}Fe -doped $\text{La}_2\text{CuO}_{4-y}$ showed that the electron capture aftereffect does not significantly broaden the lines in this Mössbauer source experiment. Broad lines might be expected for magnetic interaction weak relative to quadrupole interaction just below T_N (for La_2MO_4 , $M = \text{Cu}, \text{Co}$ at 295 K). However, it is not clear why the lines are broader at 295 K for the singlecrystal samples than for the polycrystalline samples of the same material; final heat treatments were the same.

The Mössbauer spectra for $^{57}\text{Co}(\text{La}_2\text{CoO}_{4-y})$ from 295 K to 78 K do not reflect the magnetic ordering and structural phase change reported [5] in this temperature range.

Zeeman splitting of the Mössbauer spectra for $^{57}\text{Co}(\text{R}_2\text{CuO}_4)$ is consistent with the presence of antiferromagnetic ordering of the copper moments for temperatures below about 150 K in Eu_2CuO_4 and below about 200 K in Gd_2CuO_4 [15], as had initially been hinted in susceptibility measurements [11,12]. The fitting of two sextets for Gd_2CuO_4 indicates two different types of site for the ^{57}Fe probe.

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