MOSSBAUER 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$_2$Mo$_4$ (M = Cu, Co, Ni) and R$_2$CuO$_4$ (R = Nd, Eu, Gd) were recorded at room temperature and below. Of the samples studied, only La$_2$CuO$_4$ shows a widely separated doublet at room temperature and a single clearly resolved sextet well below $T_N$.

1. Introduction

The layered perovskite La$_2$CuO$_4$ is the parent compound from which the first high-$T_c$ superconductors were obtained [1] by doping with divalent elements. La$_2$CuO$_4$ is orthorhombic at and below room temperature [2]. Oxygen-deficient La$_2$CuO$_{4-y}$ is antiferromagnetic with $T_N$ as high as 328 K [2,3], while oxygen-rich La$_2$CuO$_{4+y}$ is superconducting with $T_c \approx 30$ K [4]. La$_2$CoO$_4$ is orthorhombic at room temperature and becomes tetragonal below $\sim 135$ K; it becomes antiferromagnetic below about 275 K [5]. La$_2$NiO$_4$ is very sensitive to oxygen content, the stoichiometric compound being orthorhombic and not magnetically ordered between 95 K and 4 K [6] while La$_2$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 \( R_2CuO_{4-y} \), where \( R = Pr, Nd, Sm \) [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 \( R_2CuO_{4-y} \) 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 \( R = Eu \) [11] and Gd [12]. The compounds \( R_2CuO_{4-y} \), where \( R = \) light rare earth element Pr through Gd, differ from \( La_2MO_{4-y} \) 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 \(^{57}\text{Co-doped} \) [16] polycrystalline or single-crystal samples of layered perovskites \( La_2MO_{4-y} \) (\( M = \text{Cu, Co, Ni} \)) and \( R_2CuO_4 \) (\( R = \text{Nd, Eu, Gd} \)).

2. Experimental results

Polycrystalline samples of \( La_2MO_{4-y} \) 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 \(^{57}\text{Co} \) 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
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 ~. In mm/s, $\delta$ is the isomer shift relative to $\alpha$-Fe, $\Gamma$ is the FWHM for all lines in the spectrum, and $\Delta$ is the splitting of the doublet or $\Delta E_Q$. Error in the least significant digit is given in ( ).

| Sample          | Form | $T$ (K) | $\delta$ | $\Gamma$ | $\Delta$ | $H$ (kOe) |
|-----------------|------|---------|----------|----------|----------|-----------|
| $\text{La}_2\text{CuO}_4$ | SC   | 295     | -0.30 (5)| 0.96     | 1.68 (5) |           |
| $\text{La}_2\text{CuO}_4$ | PC   | 295     | -0.30 (1)| 0.44     | 1.76 (2) |           |
| $\text{La}_2\text{CoO}_4$ | PC   | 295     | -0.48 (5)| 1.2      | 0.0 (4)  | 434 (5)   |
| $\text{La}_2\text{NiO}_4$ | PC   | 295     | -0.39 (5)| 0.67     | 0.29 (5) |           |
| $\text{Nd}_2\text{CuO}_4$ | SC   | 295     | -0.38 (5)| 1.2      | 0.7 (1)  |           |
| $\text{Eu}_2\text{CuO}_4$ | SC   | 295     | -0.30 (5)| 0.82     | 0.65 (5) |           |
| $\text{Eu}_2\text{CuO}_4$ | PC   | 295$^a$ | -0.34 (5)| 0.64     | 0.66 (5) | 370 (10)  |
| $\text{Eu}_2\text{CuO}_4$ | PC   | 78$^a$  | -0.34 (5)| 0.30 (5) | 0.30 (5) |           |
| $\text{Gd}_2\text{CuO}_4$ | SC   | 295     | -0.46 (5)| 0.76     | 0.29 (5) |           |
| $\text{Gd}_2\text{CuO}_4$ | PC   | 295     | -0.51 (5)| 0.71     | 0.61 (5) |           |
| $\text{Gd}_2\text{CuO}_4$ | PC   | 200     | -0.39 (5)| 0.67     | 0.29 (5) |           |
| $\text{Gd}_2\text{CuO}_4$ | PC   | 180     | -0.39 (5)| 0.64     | 0.30 (5) | 290 (10)  |
| $\text{Gd}_2\text{CuO}_4$ | PC   | 78$^a$  | -0.39 (5)| 0.64     | 0.30 (5) |           |
| $\text{Gd}_2\text{CuO}_4$ | PC   | 0.14    | -0.39 (5)| 0.64     | 1.31 (5) |           |

$^a$ Sign not determined where not explicitly given.
$^b$ Ref. [14].

mg/cm$^2$ $^{57}$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 $\text{R}_2\text{CuO}_4$ ($\text{R} = \text{Eu, Gd}$) below 200 K, with a doublet and 1 or 2 sextets.

3. Discussion

$\text{La}_2\text{MO}_4$ ($\text{M} = \text{Cu, Co, Ni}$) have similar lattice constants and Cu-O octahedra; $\text{R}_2\text{CuO}_4$ ($\text{R} = \text{Nd, Eu, Gd}$) 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 $\text{La}_2\text{CuO}_4$. If in $\text{La}_2\text{CuO}_4$ this is interpreted as quadrupole splitting, then the $^{57}$Fe probe experiences much greater electric field gradient in $\text{La}_2\text{CuO}_4$ than in $\text{R}_2\text{CuO}_4$. 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 $\text{La}_2\text{MO}_4$ ($\text{M} = \text{Co, Ni}$) 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 $\text{La}_2\text{MO}_4$, $M=\text{Cu}, \text{Co}$ 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 $\text{Eu}_2\text{CuO}_4$ and below about 200 K in $\text{Gd}_2\text{CuO}_4$ [15], as had initially been hinted in susceptibility measurements [11,12]. The fitting of two sextets for $\text{Gd}_2\text{CuO}_4$ indicates two different types of site for the $^{57}$Fe probe.

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