MOSSBAUER STUDY OF MAGNETIC ORDERING IN $^{57}$Co-DOPED Eu$_2$CuO$_4$ AND Gd$_2$CuO$_4$*

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Zeeman splitting of Mossbauer spectra of $^{57}$Co doped into Eu$_2$CuO$_4$ and Gd$_2$CuO$_4$ indicates magnetic ordering of Cu moments for temperatures below about 150 K in Eu$_2$CuO$_4$ and below about 200 K in Gd$_2$CuO$_4$.

1. INTRODUCTION

Since the discovery /1, 2/ of electron superconductivity in R$_{1.85}$M$_{0.15}$CuO$_{4-y}$ (where R=rare earth, M= Ce or Th) as well as magnetic order /3/ in these compounds when the proportion of M is small, there has been widespread interest in the magnetic properties of the parent compound R$_2$CuO$_4$.

Neutron scattering studies of Eu$_2$CuO$_4$ and Gd$_2$CuO$_4$ are difficult because of large neutron absorption cross section in Eu and Gd, but magnetic susceptibility and magnetization studies have been reported on single crystal samples of these materials. These give indications that the copper moments are ordered in Eu$_2$CuO$_4$ below ~ room temperature /4/ and in Gd$_2$CuO$_4$ near 260 K /5/. $^{151}$Eu Mossbauer studies of Eu$_2$CuO$_4$ by Reagor et al. /6/ reported observing detailed temperature variation of the hyperfine magnetic field at Eu, with magnetic ordering up to temperatures above 400 K, although resolving the lines would be very difficult.

The present study of Mossbauer spectra of $^{57}$Co doped into Eu$_2$CuO$_4$ and Gd$_2$CuO$_4$ demonstrates the existence, below approximately 200 K, of hyperfine magnetic fields at $^{57}$Fe presumed to occupy the Cu site.
2. EXPERIMENTAL RESULTS

Both Eu$_2$CuO$_4$ and Gd$_2$CuO$_4$ were made by dissolving stoichiometric amounts of R$_2$O$_3$ and CuO, with co-precipitation and subsequent calcining, or alternatively by grinding together the constituents, and subsequent sintering. The final firing of the powdered samples was done in air at 900° C. X-ray powder diffraction showed the materials to be homogeneous, with lattice constants $a=3.91$ Å, $c=11.92$ Å for Eu$_2$CuO$_4$, and $a=3.90$ Å, $c=11.85$ Å for Gd$_2$CuO$_4$. (One to three unidentified very weak lines in the spectra of the samples produced by co-precipitation indicate presence of a minor secondary phase.) Each sample was pressed into a disk 1 cm in diameter and 1/2 mm thick. A drop of $^{57}$Co in dilute HCl was deposited on one face, and the disk was cooked in air at 900° C overnight. The temperature of this Mossbauer source was varied from 78 K to 295 K; the enriched (0.3 mg/cm$^2$) potassium ferrocyanide (PFC) or stainless steel (SS) absorber was at room temperature in all cases.

Mossbauer spectra are given in Figs. 1 and 2. Spectra for source

![Fig. 1. Spectra for Eu$_2$CuO$_4$ as a function of source temperature. Sample from co-precipitation.](image1)

![Fig. 2 Spectra for Gd$_2$CuO$_4$ as a function of source temperature. Sample from solid-state reaction.](image2)
temperatures below 295 K were taken with the source stationary in a Janis Supertran dewar and the absorber moving; for both source and absorber at room temperature, the source was moving and the absorber was fixed. Positive velocity is understood to mean source and absorber approaching each other. The data have been fitted with a doublet for 295 K and with a doublet and one or two sextets for temperatures below ~200 K. Intensities of the lines are allowed to be unequal for the doublets, but are chosen to be symmetric for the sextets. Linewidths (FWHM) are 0.24 mm/s for PFC absorber and 0.64 mm/s for SS absorber. Values of the hyperfine fields are given in Table 1.

Table 1

Hyperfine fields at $^{57}$Fe in $R_2CuO_4$. T is the temperature of the source. In mm/s, $\delta$ is the isomer shift relative to $\alpha$-Fe, and $\Delta$ is the splitting of the doublet or $\Delta$EQ. Error in the least significant digit is given in ( ).

<table>
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<th>Source matrix</th>
<th>Absorber</th>
<th>T(K)</th>
<th>$\delta$</th>
<th>$\Delta$</th>
<th>H(kOe)</th>
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<tr>
<td>$Eu_2CuO_4$</td>
<td>SS</td>
<td>295</td>
<td>-.34(5)</td>
<td>.66(5)</td>
<td></td>
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<tr>
<td></td>
<td>SS</td>
<td>78</td>
<td>-.72(5)</td>
<td>.30(5)</td>
<td>370(10)</td>
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<tr>
<td></td>
<td>PFC</td>
<td>295</td>
<td>-.51(5)</td>
<td>.66(5)</td>
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<tr>
<td>$Gd_2CuO_4$</td>
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<td>200</td>
<td>-.46(5)</td>
<td>.53(5)</td>
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<td>.07(5)</td>
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<td>.14(5)</td>
<td>1.31(5)</td>
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</table>

$^a$ sign not determined

3. DISCUSSION

$Eu_2CuO_4$ and $Gd_2CuO_4$ are layered perovskites like $La_2CuO_4$. But while $Eu_2CuO_4$ and $Gd_2CuO_4$ have the $T'$ phase structure with oxygen atoms square-planar coordinated about copper /7/, $La_2CuO_4$ has the "T" phase structure, with oxygens octahedrally coordinated about copper /8/. A Mossbauer study /9/ of $^{57}$Co-doped $La_2CuO_4-\gamma$ showed large quadrupole splitting for the source at room temperature (above $T_N \sim 290$ K) and a clearly resolved sextet corresponding to a single hyperfine field at temperatures below 150 K. In Mossbauer studies of $Eu_2CuO_4$ and $Gd_2CuO_4$ doped with $^{57}$Co, the doublet seen at room temperature is not so widely split as for $La_2CuO_4-\gamma$, and the spectrum becomes quite complex at 78 K.
In Mossbauer spectra taken below ~ 200 K for each type of material, for samples prepared by solid-state reaction an intense doublet persists, and two sextets can be fitted; for samples produced by co-precipitation, the doublet is far weaker, and only one sextet can be fitted. As samples made by the two methods have essentially identical x-ray powder spectra, the differences in Mossbauer spectra are attributed to probe nuclei going to different sites, with relative population depending on sample preparation. These sites may differ in number of surrounding vacancies, or in the valence of the Fe probe and the corresponding hyperfine field.

In summary, the results of this experiment are consistent with the presence of antiferromagnetic ordering of the copper moments for temperatures below about 150 K in Eu$_2$CuO$_4$, and for temperatures below about 200 K in Gd$_2$CuO$_4$.

REFERENCES

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/9/ S. Jha et al., Hyperfine Interactions, in press.